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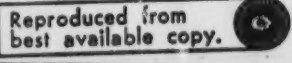
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ATMOSPHERIC FREONS AND HALOGENATED COMPOUNDS

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ABSTRACT

Ambient levels of atmospheric fluorocarbons, halogenated hydrocarbons and SF_6 are reported for various times and locations in the U.S.A. Requisite analytical and calibration procedures have been developed. A novel pulsed flow coulometry gas chromatographic analysis is described. For many compounds, laboratory test-chamber simulations of stratospheric and tropospheric irradiation have been performed. Substrate reactivity and product profiles are presented, including the effects of the presence of nitrogen oxides, humidity and a hydrocarbon mixture.

The field studies indicate compounds such as CCl_3F , CCl_2F_2 , CH_3CCl_3 and CCl_4 to be ubiquitous at generally sub ppb levels. Some tropospherically reactive compounds such as C_2Cl_4 and C_2HCl_3 are frequently measurable, while other non-ubiquitous compounds are measurable only where a reasonable source can be invoked.

The laboratory simulations establish the tropospheric stability of CCl_3F , CCl_2F_2 , CH_3CCl_3 , CCl_4 and $\text{CCl}_2\text{F}-\text{CClF}_2$. The stratospheric reactivity of CCl_3F , CCl_4 and CCl_2F_2 is confirmed.

CCl_4 is a product of C_2Cl_4 tropospheric reactions, and should be considered a secondary anthropogenic pollutant of concern in potential stratospheric ozone destruction mechanisms. Another product, COCl_2 , is of potential toxicological concern.

The adventitious labelling of air masses was used to demonstrate urban ozone transport to rural areas. It is suggested that the controversy over the origins of non-urban ozone may be resolved by simultaneously measuring halocarbons.

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LIST OF TERMS AND ABBREVIATIONS

F11	Freon 11, CCl_3F
F12	Freon 12, CCl_2F_2
F113	Freon 113, $\text{CCl}_2\text{F}-\text{CClF}_2$
PCB's	Polychlorinated biphenyls
G.C.	Gas Chromatography
E.C.	Electron Capture
P.F.C.	Pulse flow coulometry
.C.	Boundary condition
STUV	Simulated Tropospheric Ultraviolet Radiation
OCB	Ortho-chlorobiphenyl
FEP	Fluorinated ethylene propylene copolymer
PAN	Peroxyacetyl nitrate
1:1:1.T	1:1:1 Trichloroethane
T.C.E.	Trichloroethylene
P.C.E.	Perchloroethylene (Tetrachloroethylene)
V.C.	Vinyl chloride
F.S.D.	Full Scale Deflection

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SECTION I

SUMMARY AND CONCLUSIONS

There is much recent concern over the behavior and effects of halocarbons in the environment. Ambient CCl_3F and CCl_2F_2 ^(1,2) and, by analogy, other tropospherically stable compounds are suspect as precursors of stratospheric ozone-destroying chlorine atoms. Vinyl chloride has been linked to industrial angiosarcoma and is possibly mutagenic⁽³⁾. Chloroethylenes will react to form significant quantities of highly toxic phosgene and acetyl chlorides under simulated tropospheric conditions^(4,5). Chloroform and CCl_4 in Mississippi drinking water have been associated with an elevated cancer risk^(6,7). Concurrent to these findings, the research effort in ambient halocarbon measurement has justifiably increased significantly^(8,9,10,11,12,13,14,15,16). The many industrial and domestic uses of halogenated hydrocarbons and their rather large production figures (12 billion pounds in 1974 for the U.S. alone)⁽¹⁷⁾ suggest that this accelerated research effort will lead to a continual increase in the number of halocarbons routinely measured in the environment. Indeed, mass spectrometric analysis conducted on cryogenically concentrated air samples several years ago indicated the presence of a wide variety of halogenated compounds⁽¹⁸⁾.

Because of the large number of atmospheric halogenated hydrocarbons of potential interest, a selective study of a carefully chosen group representing a wide spectrum of chemical reactivities and emission patterns was clearly desirable. This approach would not only provide information of immediate relevance but also contribute to a data base for future reference as the number of halocarbons of environmental interest proliferates. Accordingly, this study has been directed towards a) development of analytical procedures for the determination of trace levels of halocarbons and SF_6 in the atmosphere, b) monitoring as many of these compounds as possible at a variety of locations in the United States, coupled with observation of their photochemical behavior in clean and "polluted" air under simulated tropospheric (and in some cases stratospheric) conditions.

1.1 Analytical Procedures

Gas chromatography, using electron capture (E.C.) detection was used throughout the study, and a number of different types of column packing were evaluated. DC 200 has been demonstrated to be an excellent packing for the separation and E.C. determination of ambient CCl_3F , CH_3I , $\text{CCl}_2\text{F}-\text{CClF}_2$, CHCl_3 , CH_3-CCl_3 , CCl_4 , C_2HCl_3 and C_2Cl_4 under isothermal (23°C) conditions. Porapak Q at 80°C , and Chromosil 310 and Carbowax 1500 at 23°C , were found acceptable for ambient CCl_2F_2 analysis. Porapak Q at room temperature is also a very good column for the separation of SF_6 and CBrF_3 . Carbowax 1500 exhibited excellent resolution of vinyl chloride at room temperature (23°C). Phosgene was found to suffer unacceptable irreversible losses in all columns studied except didecyl phthalate. This

column provided excellent resolution at 23°C and sorption losses were sufficiently small to allow accurate analysis in the sub-ppb range with frequent calibration.

The use of purge gas at low concentrations of solute leads to reduced sensitivity. This is attributable to a decrease in ionization efficiency with increasing flowrate through the EC detector. The utilization of the ionization efficiency as a confirmatory aid has been demonstrated and further applied to confirm the identity of phosgene in a simulated photochemical smog study and, accordingly, the probable tropospheric synthesis of this compound. Because of its high ionization efficiency (>75%) and instability, the latter making the preparation of calibration mixtures extremely difficult, phosgene and similar reactive strong electron absorbers are excellent candidates for coulometric analysis. Accordingly, for such compounds a detailed evaluation of gas phase coulometry and analysis of sorption kinetics was indicated. Gas phase coulometry was evaluated and used for the measurement of a number of ambient halocarbons since the method permits operation at maximum sensitivity and is absolute. Ionization efficiencies were determined for 14 compounds to range from less than 0 to 90%. Reciprocal efficiencies were verified to increase linearly with flow rate as predicted by a stirred tank reactor model. At intermediate efficiencies (40 to 60%), coulometric measurements of CCl_3F and CCl_4 exhibited a constant error of about 25% over a representative concentration range. At efficiencies greater than 90%, the percent error in coulometric analysis was less than 5% compared to primary standards. Compounds identified and measured coulometrically included CCl_3F , CH_3I , $\text{CH}_3\text{-CCl}_3$, CCl_4 , CHCl=CCl_2 and $\text{CCl}_2=\text{CCl}_2$.

For the absolute analysis of reactive electron-absorbing compounds which undergo decomposition in a G.C. column, a novel modification of gas phase coulometry, termed Pulse Flow Coulometry (PFC) was developed and used successfully. Comparing this technique against permeation tube standards, an error of less than 15% was easily achieved when ionization efficiencies were greater than 75%. At ionization efficiencies greater than 85%, this error could be reduced to 4%. The electron capture detector response to phosgene was comparable to that to carbon tetrachloride, one of the strongest known electron absorbers. It was demonstrated that ppb mixtures of phosgene in air are quite stable in the presence of moisture and undergo rapid heterogeneous decay on surfaces. PFC should be useful for the analysis of any unstable electron absorber (e.g. peroxyacetyl nitrate [PAN], chlorine dioxide, trichloroacetyl chloride) in air and offers a wide scope of application in air pollution and industrial hygiene.

1.2 Atmospheric Behavior of Halocarbons

The halogenated compounds studied are primarily anthropogenic and exhibit wide fluctuations in concentration as a function of location and meteorological factors. However, typical halocarbon ranges at different locations can be inferred from the data base presented here. CCl_3F , CCl_2F_2 , CH_3CCl_3 and CCl_4 were found to be ubiquitous atmospheric constituents. Their concentrations in the rural areas were typically in the sub-ppb range and

urban concentrations were generally much higher. The first three compounds are of known anthropogenic origin but the CCl_4 atmospheric budget is inconsistent with direct anthropogenic emissions.

Our studies support the possibility of the formation of some CCl_4 in the troposphere by solar-induced photochemical reactions of chlorinated alkenes. Such a process is of major importance in the consideration of ozone destruction by chlorine atoms, since our laboratory simulation studies indicate that CCl_4 , like the fluorocarbons, is tropospherically stable but would break up under stratospheric conditions. Chlorinated alkenes should therefore be included in any evaluation of possible ozone destruction. The ubiquitous compounds and $\text{CCl}_2\text{F}-\text{CClF}_2$ are tropospherically stable and will experience their ultimate fate in the stratosphere. Among the tropospherically reactive halocarbons, C_2Cl_4 and C_2HCl_3 should lead to the formation of large quantities of phosgene in the atmosphere which may have a potentially significantly impact. Methyl iodide was measurable generally only near the ocean, supporting its origin there. SF_6 and vinyl chloride were usually measurable only where a reasonable nearby source could be involved.

It has been demonstrated that halocarbons can be used as excellent tracers of urban transport. Additionally, studies of the temporal and spatial distributions of halocarbons in non-urban areas should help to differentiate between the natural synthesis, urban transport and stratospheric injection of ozone.

Because of the possible stratospheric ozone destruction by stable halocarbons, the toxicity of phosgene, the indicated carcinogenicity of vinyl chloride and its structural similarity to other ambient chloro-ethylenes, and the unknown long-term effects of halogenated compounds and their reactive products, further research in this area is clearly warranted.

SECTION II

GENERAL INTRODUCTION

This project had as its inception a literature search which was initiated in the Spring of 1971 to estimate worldwide production of industrial chemicals and the percentages of them emitted into the atmosphere and to consider the tropospheric removal mechanisms and fates of these materials. As a result of this search it was determined that in terms of the quantities of materials estimated to be emitted on the one hand and the possible environmental impact of these primary pollutants or their degradation products on the other hand, continuation of this effort in the direction of ambient monitoring and of tropospheric and stratospheric simulation experiments was justified. It was especially clear from the initial literature search that there was a paucity of data on the environmental fates of halocarbons in general and fluorocarbons in particular. This followed and was understandable from the almost complete lack of pertinent information on the atmospheric concentrations of these materials and on their sinks and on the identity and kinetics of their reactants, intermediates and products of photochemical degradation. As a result, a proposal was submitted to E.P.A. in 1972 to provide requisite information for subsequent meaningful toxicological and environmental impact studies.

The initial proposal listed 19 chemicals, most of which were halogenated hydrocarbons. Production figures taken from the pertinent U.S. Tariff Commission Reports were listed, and from these, projections on worldwide sales in the categories of aerosol propellants, refrigerants, plastics, solvents, blowing agents and miscellaneous were developed. It was shown that 99% of the world's fluorocarbon sales were accounted for by only 5 Freons and plastics, and that major fluorocarbon usage was in aerosol propellants.

Various possible sinks for the fluorocarbons were considered, viz: dissolution in the ocean, washout by rain, escape into the stratosphere, microbial utilization, absorption at the earth's surface, air breathers and plants and tropospheric photochemical reactions. Dissolution in the oceans was shown to be insignificant from a simple consideration of Henry's Law. Washout by rain was similarly insignificant. Microbial utilization and absorption at the earth's surface were similarly ruled out, and later a detailed analysis of mechanical and biological air breathers showed them to be insignificant sinks. The possibility of sinks involving stratospheric and tropospheric photochemical reactions and plants was left open. Indeed the only hint at the relative importance of these possibilities was provided by a few isolated measurements of atmospheric concentrations of F-11 and SF₆ by Lovelock⁽⁸⁾. He reported the F-11 background concentration as 10⁻¹¹ v/v. Computing the total worldwide emissions of F-11 from 1958 to the time of Lovelock's measurements gave a total worldwide tropospheric emission of F-11 during the period of 1958 to July 1970 as 3376x10⁶ pounds. Comparing this with the

actual "tropospheric loading" calculated from Lovelock's background measurements of 553×10^6 pounds it was concluded that important sinks for fluorocarbons existed. The known tropospheric/stratospheric turnover rate could only account for a fraction of this deficit strongly supporting the existence of tropospheric photochemical sinks involving reactive hydrocarbons, oxides of nitrogen, O_3 and their associated intermediates. Also, a more extensive study was indicated because of the significance of possible build-up of these compounds towards such factors as toxicological effects, global greenhouse effect, and their potential use as tracers of air masses. Accordingly the proposed research protocol included tropospheric photochemical reactivity studies of saturated halocarbons as well as those unsaturated halocarbons emitted in significant quantities and expected to be reactive. Because, despite the available ambient measurements, all theoretical considerations would argue against reaction of the saturated halocarbons in the troposphere, the original proposal also included an elaborate plan to study stratospheric reactivity of many of these compounds, with emphasis on the fluorocarbons. Indeed, literature existed that the halocarbons would undergo photolytic decay at wavelengths corresponding to stratospheric conditions. E.P.A. did not fund this stratospheric halogenated hydrocarbon aspect of the proposal. Some modest studies were however carried out and are reported here. The role of plants as possible sinks was not considered in this study.

Also included with the fluorocarbons for study were such possibly carcinogenic compounds as vinyl chloride, CCl_4 and trichloroethylene and the teratogenic P.C.B.'s. Product identification was also considered to be an important feature because of the possibly significant toxicity of such expected products as phosgene and the chloroacetyl chlorides. The role, if any, that reactive halogenated compounds play in the classical photochemical smog cycle was also a feature of the work.

In order to approach the assessment of the fates of these compounds the project involved three phases running essentially concurrently. (1) A continuation of the literature survey to upgrade our information on emissions data and possible sinks. (2) A program of ambient measurements to provide tropospheric concentrations of the compounds and to estimate their atmospheric budget and removal mechanisms. (3) Laboratory studies in which controlled simulation of tropospheric and stratospheric photochemical conditions were used. It was necessary to develop analytical procedures and techniques usable at the very low concentrations (10^{-9} to 10^{-12} v/v) anticipated, as a prelude to the required program of ambient measurements. Also, significant research and development effort had to be expended on the preparation, irradiation and sampling of gas mixtures in a fashion consistent with optimum simulation of ambient conditions.

The arrangement of this report is as follows. Following this General Introduction is a section on Literature Review, with subsections on the major compounds studied. Then follows the Experimental Section which

includes all the standard analytical procedures used in this work. A considerable portion of this project involved development of gas chromatographic procedures and columns for the analysis of very low levels of halocarbons and related compounds. While a brief account of the gas chromatographic instrumentation used appears in the Experiment Section, a complete account of this analytical development is given in the next section, "Gas Chromatographic Analytical Procedures for Trace Levels of Halocarbons and SF₆."

Section VI presents the results and discussion of our ambient measurements, with subsections devoted to "ubiquitous" and "non-ubiquitous" halocarbons, their variability, and general comments pertaining to each of the locations studied. Section VII describes the photochemical reactivity studies with subsections for each compound.

SECTION III

LITERATURE REVIEW

INTRODUCTION

An important aspect of this work was a continuing review of available literature on the sources, reactions, fates and levels of these compounds. Presented in this section are references to work of especial significance to this project.

As mentioned in the General Introduction, the earliest report on background concentrations of any of these compounds was that of Lovelock⁽⁸⁾. He reported CCl_3F and SF_6 values in southwest Ireland of 10^{-11} and 2.9×10^{-14} (v/v), respectively, as representative of northern hemispheric background concentrations. Air passing over the continent from an easterly direction exhibited corresponding concentrations approximately an order of magnitude higher for both. Atmospheric concentrations ranging from 0.05 to 0.17 ppb CCl_3F in Bowerchalke, England, were also reported by Lovelock⁽¹²⁾ for the period October 1970 to October 1971. No significant seasonal variation of CCl_3F was observed. Lovelock et al.⁽¹⁰⁾ also reported mean aerial concentrations of 0.049 CCl_3F , 0.001 CH_3I and 0.071 CCl_4 ppb (v/v) over the north and south Atlantic Ocean. Hester et al.⁽⁹⁾ reported CCl_3F and CCl_2F_2 levels at various indoor and outdoor locations in the Los Angeles Basin. Ambient CCl_2F_2 and CCl_3F levels were in the range of 0.1 to 1.25 ppb and 0.05 and 147 ppb respectively. Simmonds et al.⁽¹⁶⁾ in a three-day study reported levels of CCl_3F , CCl_4 , CH_3CCl_3 and C_2Cl_4 in the Los Angeles Basin. The reported concentration (ppb) ranges were 0.11-2.2 for CCl_3F , 0.1-1.63 for CCl_4 , 0.01-2.3 for CH_3CCl_3 and 0.1-4.2 for C_2Cl_4 .

Wilkniss, Lamontagne, Larsen and Swinnerton⁽¹³⁾ reported CCl_4 and F-11 concentrations over the ocean of about 80 and 60 ppb respectively. Recently Lovelock⁽¹⁹⁾ reported concentrations of F-11, F-12, CHCl_3 , 111T, CCl_4 , TCE, and PCE in western Ireland (June, July 1974) and over the north Atlantic Ocean (October 1973). Except for TCE, the values in the two locations were approximately the same, namely:

F-12	about 100-115 ppt.
F-11	about 80-90 ppt.
CHCl_3	about 19-27 ppt.
111T	about 65-75 ppt.
CCl_4	about 111-138 ppt.
TCE	<5 in north Atlantic 15 in Ireland
PCE	21-28

(It should be noted that the F-11 values are about an order of magnitude greater than his earlier report.)

He also reported vertical profiles of F-11 and CCl_4 over central England (June 6, 1974), demonstrating their presence in the tropopause and lower

stratosphere. Saltzman et al.⁽²⁰⁾ irradiated mixtures of reactive atmospheric pollutants, CBrF_3 , SF_6 and C_4F_8 with simulated sunlight and attributed the observed loss of less than 2% per day for the above compounds to permeation through the walls of the film bags. Hester et al.⁽⁹⁾ provided support for the short-term tropospheric stabilities of CCl_2F_2 and CCl_3F based on smog simulation studies. Wilson⁽²¹⁾ reported the photo-reactivity of trichloroethylene and its possible involvement in the photochemical smog phenomenon. Molina and Rowland⁽¹⁾ and Cicerone et al.⁽²⁾ have recently suggested the possible destruction of the stratospheric ozone layer by chlorine-atom-propagated chain reactions initiated by the photolysis of CCl_3F and CCl_2F_2 . Experimental smog chamber data supporting the assumed long-term tropospheric stability of these compounds, however, is insufficient. No data at all exist on the tropospheric stability of many other chlorinated compounds present in the troposphere at comparable concentrations to CCl_3F and CCl_2F_2 .

SPECIFIC COMPOUNDS

3.1 F-11 and F-12

3.1.1 Use and Production -

Freon 11 and Freon 12 are used widely in household and industrial environment with extensive application as refrigerants, propellants for perfumery and medicinal products, insecticides and fire repellants. They are being used more and more in space technology and their worldwide uses are even expected to increase as underdeveloped countries become more and more industrialized. Dupont (1972) estimated that 99% of the world's fluorocarbon sales are accounted for by Freon 11, 12, 22, 113 and 114. Freon 11, 12 and 114 are the major fluorocarbons used for aerosol propellants.

The use of the Freon 11 and Freon 12 in household and industrial application is increasing at a significant rate as seen from U.S. Production Data (1965-1973).

Table 1. U.S. PRODUCTION OF F-12 AND F-11
(U.S. Tariff Commission Reports)
(Units of 1000 pounds)

Year	Freon-12	Freon-11
1965	271,408	170,461
1966	286,326	170,350
1967	309,668	182,216
1968	325,625	204,418
1969	363,658	238,518
1970	375,406	244,472
1971	389,580	257,899
1972	439,224	299,583
1973	488,831	333,773

The 1972 world production rates for Freon 11 and Freon 12 are about 0.3 and 0.5 million tons per year respectively⁽²²⁾ and are steadily increasing. By the nature of the use of these compounds they are emitted to the troposphere in significant quantities.

3.1.2 Sinks -

An all inclusive list of possible sinks for any tropospheric constituent would include the following:

- (1) Dissolution into the ocean according to Henry's Law followed by hydrolysis.
- (2) Washout by rain.
- (3) Escape through the tropopause gaps to the stratosphere.
- (4) Microbiological utilization at earth surface.
- (5) Absorption at earth surface.
- (6) Sorption and/or utilization, and/or degradation by plant life and biological and mechanical air breathers.
- (7) Stratospheric and tropospheric photochemical and/or thermal reactions.

Careful analysis indicates that due to such properties as chemical inertness, low solubility in water, slow hydrolysis rate, lack of data to indicate biodegradability and low partial pressure of fluorocarbons, the aforementioned sinks numbered 1, 2, 4 and 6 are very insignificant in terms of the total amount of Freon 11 and Freon 12 they would remove from the troposphere. Freon 11 and Freon 12 are not very soluble in water and therefore not removed by rainouts in the troposphere⁽¹⁾. The relative insolubility in water together with the chemical stability, particularly towards hydrolysis⁽²⁵⁾ indicates that these molecules will not be rapidly removed by dissolution in the ocean, and measurements made indicate equilibrium between the ocean surface and air. Therefore a major sink other than photolysis cannot be inferred⁽¹⁰⁾. Based on the evidence presented in this discussion tropospheric and thermal reactions or stratospheric flux must be considered as the significant removal mechanism.

3.1.3 Reactivity Studies -

Hester⁽⁹⁾ reported long term photolysis studies on Freon 11 and Freon 12 in which 76 ppb Freon 11 and 2.3 ppb Freon 12 were irradiated in Los Angeles air. However, after almost 2 months photolysis, no observation of a chemical reaction of either Freon 11 or Freon 12 was discovered. A second scheme of experimentation was pursued in which a photolysis study was run analogous to that previously stated except that 0.1 ppm NO₂ was added to the system. The photolysis was for 7 hours and the experimenters noted no indication of any chemical reaction, as indicated by no decrease in either fluorocarbon concentration. The photolysis studies were done in a 20 liter reaction flask surrounded by 11 "Black Light" Type U.V. lamps.

3.1.4 Ambient Measurements -

Ambient measurements of Freon 11 and Freon 12 have indicated their presence in the atmosphere. Lovelock⁽⁸⁾ reported a measured concentration exceeding 10^{-11} by volume over Ireland. Measurements of CCl_3F have also been made in several parts of the world. Lovelock et al.⁽¹⁰⁾ reported ambient atmospheric measured concentration of Freon 11 for the Los Angeles Basin, Europe, and other parts of the Atlantic. Based on these measurements they estimated a background concentration of 1×10^{-11} v/v. Wilkniss et al.⁽¹³⁾ measured trace gases in the atmosphere over the north and south Pacific Ocean. Goldberg et al.⁽¹⁵⁾ reported average atmospheric concentrations of 2.9×10^{-10} and 3.2×10^{-9} for CCl_3F and CCl_2F_2 respectively. Simmonds et al.⁽¹⁶⁾ measured the concentration of four halogenated hydrocarbons throughout the air over the Los Angeles Basin in which they reported average concentrations of .55 ppb for CCl_3F . Based on ambient atmospheric measurements of Freon 11 and Freon 12 in the greater Los Angeles Basin, it was found⁽⁹⁾ that concentrations of Freon 11 and Freon 12 in homes range from .22 to .12 ppb for Freon 11 and 0.3 to 510 ppb for Freon 12.

It is of particular interest to note that this study indicated that the levels of Freon 11 and Freon 12 were significantly higher in homes than in ambient air samples.

3.2 Perchloroethylene

3.2.1 Use and Production -

In January 1963 there were an estimated 36,500 dry cleaning plants in the United States resulting in approximately one plant for every 2500 people in urban areas and one for each 500 people in the country in general⁽²⁴⁾. There were also 7300 self service "coin operated" dry cleaning stores containing about 50,000 machines. It was also estimated at that time that the dry cleaning industry alone consumed 25 million gallons of perchloroethylene per year. It is of importance to note that because of zoning laws against petroleum solvents, the number of plants utilizing perchloroethylene is increasing at a rapid rate, and that for reasons of convenience dry cleaning plants are located at or near centers of high population density. Estimates indicated that in 1968 the dry cleaning industry accounted for 75% of the reported sales of perchloroethylene⁽²⁵⁾. The remainder probably also results in significant emission of the compound in urban atmospheres. The following table indicated the increase in the production of perchloroethylene from 1965 to 1972.

Table 2. SYNTHETIC ORGANIC CHEMICALS, U.S. PRODUCTION AND SALES
(U.S. Tariff Commission Reports)
(Units of 1000 pounds)

1965	429,354	1969	635,251
1966	462,678	1970	706,896
1967	532,980	1971	704,747
1968	635,484	1972	734,216

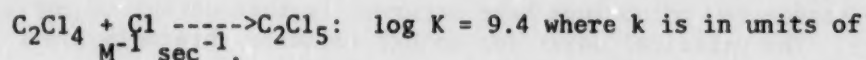
The above report indicated an increase of approximately 70% in the U.S. production of perchloroethylene over this period.

3.2.2 Reactivity Studies -

Huybrechts et al.⁽²⁶⁾ studied the oxygen inhibited photochlorination and chlorine sensitized oxidation of perchloroethylene and pentachloroethane at 353.3°K and 373.4°K. The reaction was initiated by light at 4358Å in which the rates of chlorination of both compounds were given. It was observed that the rate of chlorination decreased progressively on adding increasing amounts of oxygen and at the same time a chlorine photo-sensitized oxidation took place. Analysis of products in experiments carried to completion showed that 85% (±5%) of the oxidized perchloro and pentachloroethane appears as tetrachloroacetyl chloride and 15% (±5%) as phosgene corresponding to the overall reaction:



Trace quantities of carbon tetrachloride (.3%) and tetrachloroethylene epoxide (.1%) were also detected. Horowitz et al.⁽²⁷⁾ studied the kinetics of the photochemically initiated reaction between tetrachloroethylene and pentane. Experiments were conducted at 25°C and energy was provided by a high pressure mercury lamp. The reaction resulted in the formation of pentyltrichloroethylene and HCl, and the rate constant for the rate-determining step was estimated at $6.6 \times 10^2 \text{ sec}^{-1}$. Goldfinger et al.⁽²⁸⁾ studied the gas phase photochlorination of perchloroethylene with methane, methyl chloride, methylene chloride, chloroform, and pentachloroethane in a static system between 385° and 490°K, in which they utilized light of different intensities in an effort to obtain "satisfactory sensitivities." Reaction rates were followed monometrically and photometrically allowing the following rate constant to be measured:



Dusoleil et al.⁽²⁹⁾ investigated gas phase photochlorination of perchloroethylene and pentachloroethane in a static system in which light of

4047 - 4358Å was utilized, and the reaction temperature was 418.80°K. They also conducted other experiments at temperatures up to 564°K. There is no documentation of smog reaction studies performed on perchloroethylene.

3.2.3 Ambient Measurements -

Available data on ambient background concentrations of perchloroethylene are in conflict. Tohura Kuriyang⁽³⁰⁾ reported 1 ppm C₂Cl₄ as ambient background concentration. His reported data was obtained using a specially designed non-dispersive ultra violet absorber. However, Reid et al.⁽³¹⁾ reported detection and measurements of ambient concentrations of C₂Cl₄ below 1 ppm. Williams⁽³²⁾ utilizing an electron capture detector, reported background atmospheric concentrations of perchloroethylene to be less than 1 ppb. Murray et al.⁽¹⁴⁾ made ambient measurements of C₂Cl₄ in rural areas of Britain and away from large towns in which an attempt was made to examine the environmental distribution of the aliphatic chloro-compounds in which significant amounts of these compounds were detected, particularly in air from towns and cities, as would be expected. Simmonds et al.⁽¹⁶⁾ conducted measurements of atmospheric halocarbons throughout the Los Angeles area in which he reported average concentrations of 0.125 ppb of perchloroethylene. Lillian and Singh⁽¹¹⁾ have reported background concentrations of 0.12 ppb C₂Cl₄ in the New Brunswick area. This was determined by gas phase coulometry.

3.3 Methyl Iodide

3.3.1 Sources, Uses and Toxicity -

Methyl iodide is a colorless liquid with a sweet ethereal odor. On exposure to light a light brown color develops due to the liberation of iodine. It is used mainly in the laboratory as a methylating agent and as an intermediate in the chemical industry. It has been used in fire extinguishers, as a vesicant in chemical warfare, in the process of stone carving and it is used in microscopy as an embedding agent due to its high index of refraction. Methyl iodide is prepared by the reaction of dimethyl sulfate and sodium iodide in a still⁽³⁵⁾. An old commercial method involved the burning of seaweed^(34,35).

Methyl iodide is not used extensively and consequently, few cases of poisoning have occurred. One was reported in 1901, in a dye factory⁽³⁶⁾. The symptoms were vertigo, diplopia, ataxia, and the patient swaying as if drunk. When delirium and mania ensued, treatment in a mental hospital was necessary but the mental dullness persisted. In 1940, an exposure in a methyl iodide factory caused nausea, vomiting, diarrhea, vertigo, slurred speech, visual disturbances, tremor, drowsiness and then coma. Another reason few poisonings have occurred is that methyl iodide is lacrimatory. The principal basis for methyl iodide's threshold limit value of 5 ppm is its tendency to sensitize the skin.

Methyl iodide is considered ten times as acutely toxic as carbon tetrachloride by the American Conference of Governmental Industrial Hygienists⁽³⁷⁾. Figure 1 includes the sales of CH₃I for the period 1967 to 1973. Based on studies in the literature^(10,16) and on our own sampling⁽³⁸⁾, the typical concentration of CH₃I in air is 0.001 ppb.

From the sales figures and the scarcity of ambient data, one can only estimate the residence time. It is obvious that methyl iodide has a natural source. Lovelock et al.⁽¹⁰⁾ measured methyl iodide in and over the Atlantic Ocean. They suggest that the sea is the source of atmospheric methyl iodide. The atmospheric residence time has been estimated at 50 hours suggesting an annual production of 90 billion pounds⁽¹⁰⁾. A possible reaction of atmospheric sea salt and methyl radicals can be the source of CH₃I. Biological methylations in seaweed and marine algae should also be considered as a possible natural source of methyl iodide.

3.3.2 Reactivity Studies -

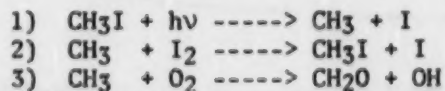
Investigations of the photochemical reactions of methyl iodide are well documented in the literature. Bates and Spence⁽³⁹⁾ were the first to look into the photooxidation of gaseous methyl iodide. Their work, noting that the absorption spectrum of methyl iodide (Figure 2) was continuous above 2000Å, indicates that decomposition is the primary effect of light absorption. They varied the concentrations of oxygen from 10 to 600 torr, methyl iodide from 10 to 100 torr, and light intensity from 30% to 100% at 2537Å. The results of their experiments point to a linear relationship between light intensity and reaction rate.

$$\frac{-d(\text{CH}_3\text{I})}{dt} = \frac{2 A k_1 (\text{O}_2) k_3}{(I_2) k_2 + (\text{O}_2) k_3}$$

where $A = I_0 (1 - e^{-\alpha(\text{CH}_3\text{I})})$
 I_0 = intensity at 2537Å

and α = molar extinction coefficient at 2537Å

k_1 , k_2 and k_3 being the rate constants determined from the reactions:



The Quantum yield was found to be 2.

At these relatively high concentrations, side reactions of the products interfere with the elucidation of the quantum yield of the primary photolysis. Their experimental data fit the following expression for the decomposition rate of methyl iodide:

$$\frac{-d [\text{CH}_3\text{I}]}{dt} = \frac{k(1 - e^{-0.047[\text{CH}_3\text{I}]}) [\text{O}_2]}{12.3 + [\text{O}_2]}$$

Figure 1
U.S SALES OF HALOCARBONS
1967 - 1973

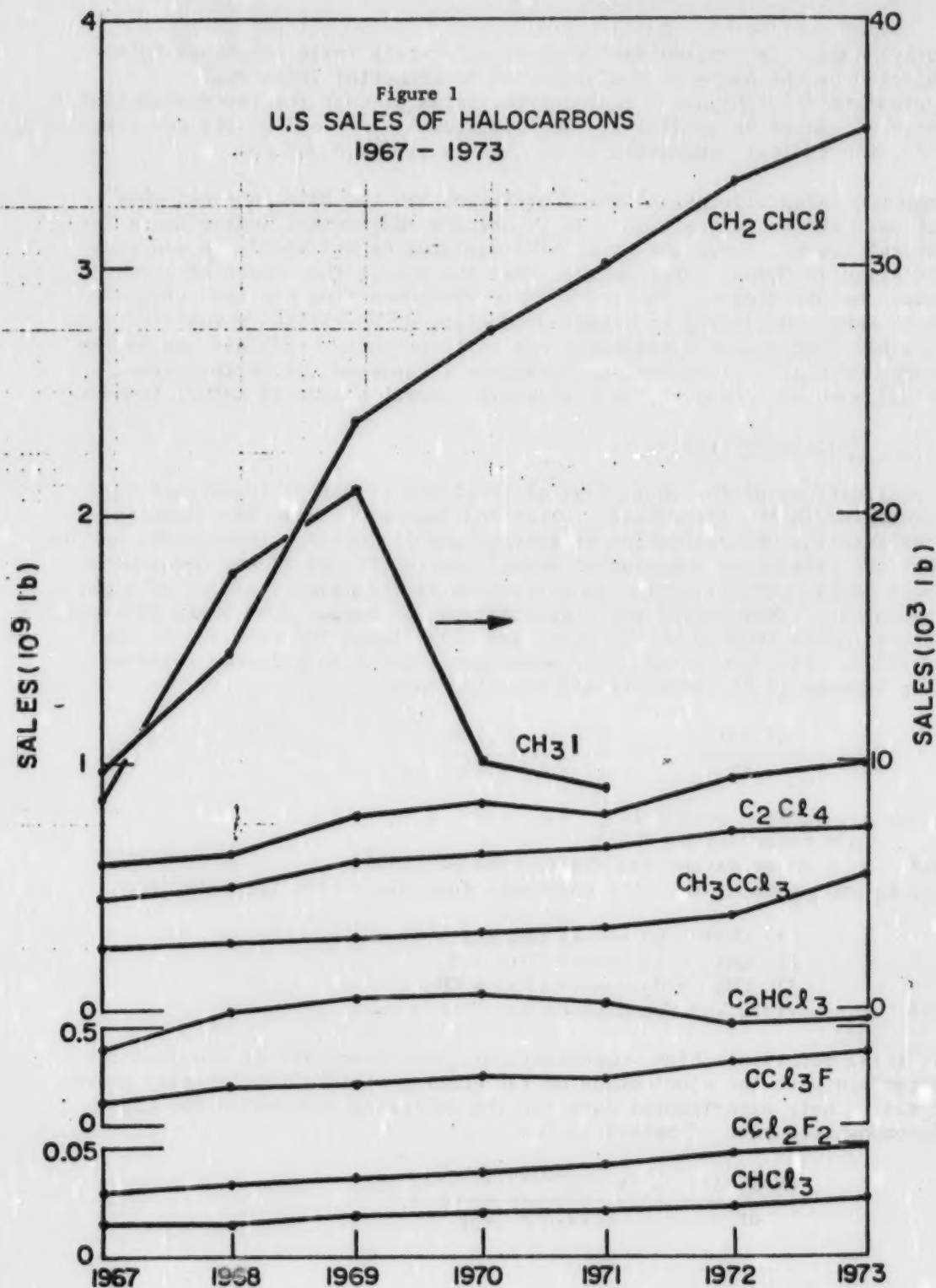
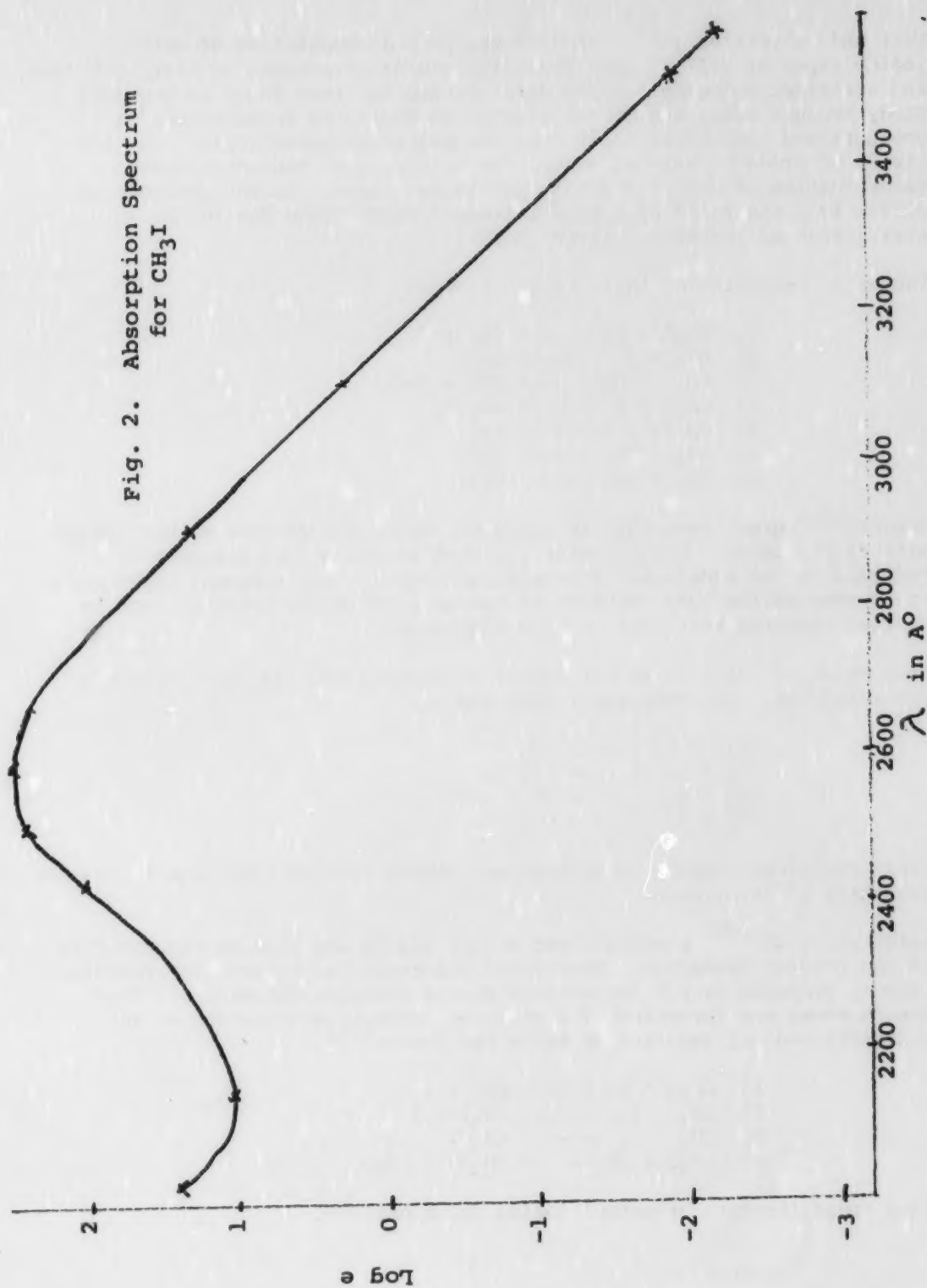
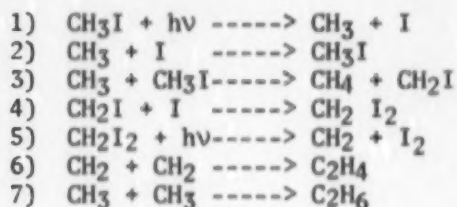


Fig. 2. Absorption Spectrum
for CH_3I



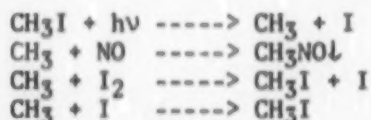
West and Schlessinger⁽⁴⁰⁾ studied the photodecomposition of methyl iodide vapor at 2537Å. They found low yields of methane, ethane, ethylene, and methylene diiodide. Their data changed the rate found in previous study because Bates and Spence assumed no iodinated hydrocarbons as products and simplified their reaction mechanism accordingly. The low yields of products were accounted for by the great tendency towards recombination of methyl radicals and iodine atoms. In the presence of silver foil the yield of ethane increased forty times due to the abstraction of iodine as silver iodide.

The major reactions of their mechanism were:



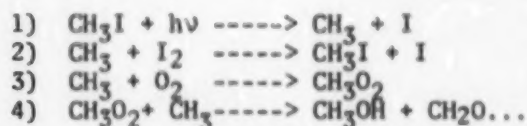
Iredale⁽⁴¹⁾ questioned the low yield of iodine and reacted methyl iodide with nitric oxide. Nitric oxide was used to detect the presence of radicals in the reactions of organic molecules. The compound CH_3NO seems to be removed from the reaction system as a solid and takes no part in further chemical reactions at room temperature.

Absorption of light by methyl iodide to form an excited CH_3I^* molecule was ruled out. His reaction scheme was:



Other reactions leading to methane and ethane were excluded due to the low frequency of occurrence.

Leighton et al.⁽⁴²⁾ photooxidized methyl iodide and studied the kinetics of the product formation. They found discrepancies between the reaction schemes proposed by earlier workers due to experimental errors. They hypothesized the formation of a peroxide intermediate instead of an hydroxide radical proposed by Bates and Spence⁽³⁹⁾.



They found the rate of methyl iodide decomposition:

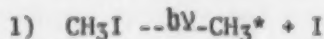
$$\frac{-d(\text{CH}_3\text{I})}{dt} = \frac{I[\text{O}_2]}{k_2 + 2k_3 [\text{I}_2] + [\text{O}_2]}$$

Where the maximum quantum yield is unity.

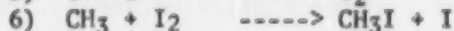
This discrepancy in quantum yields was researched further by Iredale and McCartney⁽⁴³⁾. They found that only when the nitric oxide pressure is lower than 50 torr do the back reactions: $\text{CH}_3\text{I} + \text{I}_2 \rightleftharpoons \text{CH}_3\text{I} + \text{I}$
 $\text{CH}_3\text{I} + \text{I} \rightleftharpoons \text{CH}_3\text{I}$

begin to lower the quantum yield. When the pressure of nitric oxide is greater than 50 torr the quantum yield approaches unity. Their experiments, however, were performed over a spectrum from 2500 to 2700Å, and weighted averages had to be employed in their intensity calculations.

Shultze and Taylor⁽⁴⁴⁾ postulated the "hot" methyl radical formation in the approximately 50 - 60 kcal/mole greater than the carbon-iodine bond strength of 54 kcal/mole. The reaction mechanism they proposed was:



where CH_3^* represents a methyl radical with excess energy of 32 kcal/mole.



Reaction (2) is the sole source of methane production. They found an apparent activation energy for methane production of zero in the temperature range of 40° - 100°C. Ordinarily 8 kcal/mole of energy would be needed to produce methane. Hence, an increase in temperature would vary the amount of methane produced. This is not the case. The quantum yield of methane production is a low 0.003 due to the fact that reaction (3) takes place more readily. Unless the reactants at the instant of collision are oriented in the right way, the "hot" radical will merely lose kinetic energy in collision with a third body (3). The methyl radical, having lost its excess energy will most likely react in (6), but if iodine can be removed sufficiently rapidly by fixation with silver as silver iodide, reaction (4) would become appreciable.

Willard⁽⁴⁵⁾ explains that a "hot" radical is one which has been born with energy much in excess of the average energy of the surrounding molecules and has not yet reached thermal equilibrium with them. If it reacts chemically before becoming thermalized, the reaction is a "hot" reaction. A typical hot radical can carry its excess kinetic energy through only a few collisions.

Although hot radicals are probably produced in many photochemical dissociations, only a few examples of their reactions have been reported. This is due to the low quantum yields of hot reactions.

The quantum yield for the reaction of hot methyl radicals with methyl iodide is 0.003 for radicals formed at 2537Å, whereas it is 0.03 for radicals formed at more energetic 1849Å light. Most photochemical reactions have been studied under conditions where the rate of thermal reaction is sufficient to mask the rate of a hot reaction. This means that a high light intensity source is needed to produce observable hot radical reactions.

Martin and Noyes⁽⁴⁶⁾ investigated the reactions of methyl radicals with oxygen. They found formaldehyde to be one of the principal products of methyl iodide and oxygen mixtures at room temperature. Ethane was not found among the products when oxygen was present and quantities of carbon dioxide and carbon monoxide result ultimately from reaction of methyl radicals with oxygen.

Hudson, Williams and Hamill⁽⁴⁷⁾ studied the moderation of hot methyl radicals in the photolysis of methyl iodide. Moderators are inert gases added to the reactions to physically decrease the rate of production of a product, in this case, methane. The investigators used neon, argon, helium and carbon dioxide as moderators and found methane production decreased by a constant factor, yet this decrease was independent of temperature change. This experiment strengthened the hot radical hypothesis of Shultz and Taylor.

Souffie, Williams and Hamill⁽⁴⁸⁾ continued the study of hot radical reactions. They measured rates of production of ethane, methane and iodine as functions of pressure, temperature, iodine concentration, various moderators and reactive substances added to obtain a better picture of the hot radical reaction.

Their reaction mechanism:

- 1) $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3^* + \text{I}$
- 2) $\text{CH}_3^* + \text{CH}_3\text{I} \rightarrow \text{CH}_4 + \text{CH}_2\text{I}$
- 3) $\text{CH}_3^* + \text{RH} \rightarrow \text{CH}_4 + \text{R}$
- 4) $\text{CH}_3^* + \text{CH}_3\text{I} \rightarrow \text{C}_2\text{H}_6 + \text{I}$
- 5) $\text{CH}_3^* + \text{CH}_3\text{I} \rightarrow \text{CH}_3\text{I} + \text{CH}_3$
- 6) $\text{CH}_3^* + \text{M} \rightarrow \text{CH}_3 + \text{M}$
- 7) $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$
- 8) $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$
- 9) $\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I}$
- 10) $\text{CH}_2\text{I} + \text{I}_2 \rightarrow \text{CH}_2\text{I}_2 + \text{I}$
- 11) $\text{I} + \text{I} + \text{M} \rightarrow \text{I}_2 + \text{M}$

The rates of production of ethane and iodine decrease during the early stages of the photolysis. Addition of iodine further decreases the ethane rate to a limiting rate. This limiting rate is independent of further changes in iodine concentration. The authors attribute this production of ethane to the hot radical reaction (4). The quantum yield of "hot ethane" is 3.6×10^{-4} .

The authors also suggest that "hot" ethane production is the result of

excess translational energy in the methyl radical while methane production may be the result of excess internal energy. In all their experiments, the extent of decomposition of methyl iodide sample (present at 150-200 torr) was less than 5%.

Christie's work⁽⁴⁹⁾ was to investigate the photochemical oxidation of methyl iodide under conditions such that oxygen molecules were competing with iodine molecules and/or iodine atoms for reaction with methyl radicals, and thus to obtain information about the kinetics of the reactions involved. She found that in excess oxygen, the photochemical reaction was zero order, i.e. the amount of iodine produced was directly proportional to the time of irradiation. The quantum yield of iodine is 0.5 since her experiments showed that oxygenated products did not contain iodine. The reaction mechanism was:

- 1) $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}$
- 2) $\text{CH}_3 + \text{I}_2 \rightarrow \text{CH}_3\text{I} + \text{I}$
- 3) $\text{CH}_3 + \text{O}_2 \rightarrow \text{products}$
- 4) $\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$
- 5) $\text{I} + \text{I} + \text{M} \rightarrow \text{I}_2 + \text{M}$
- 6) $\text{CH}_3 + \text{I} \rightarrow \text{CH}_3\text{I}$

where the reaction (6) is negligible compared with reaction (2) in the methyl iodide plus oxygen system. Note also the reaction (4) is third order.

McKellar and Norrish⁽⁵⁰⁾ combusted methyl iodide under slow and explosive conditions. Hydroxyl radicals and formaldehyde were among the products formed. Their data indicates the reaction $\text{CH}_3 + \text{O}_2 \rightarrow \text{H}_2\text{CO} + \text{OH}$ occurs. The significance of this reaction in the ambient atmosphere is slight, however, since explosive conditions are highly unlikely.

Heicklen and Johnston⁽⁵¹⁾ reacted low concentrations (260 ppm) of methyl iodide in oxygen with ultraviolet radiation above 2200Å. Their measurements were made by leaking the reaction mixture directly into the electron beam of a mass spectrometer during photolysis. Their very complex reaction mechanism involves 24 steps to include such reaction products as: I_2 , H_2CO , CH_3OH , CH_3OOH , H_2O , CO_2 , CHOOH , CH_3OOCH_3 and CH_3OI . A number of free radicals are also involved in the system. The best way to present these is in the following chart which shows the source and fate of free radicals and source of products in the proposed complex mechanism⁽⁵¹⁾.

abstraction reaction, $\text{CH}_3^* + \text{CH}_3\text{I} \rightarrow \text{CH}_4 + \text{CH}_2\text{I}$. This fact plus the more efficient reaction, $\text{CH}_3^* + \text{M} \rightarrow \text{CH}_3 + \text{M}$ account for the low methane yields.

Gilbert, Lambert and Linett⁽⁵⁴⁾ thoroughly explored the photolysis of $\text{CH}_3\text{I} + \text{NO}$ mixtures. Their mass spectrometer was sampling directly from the reacting system. Their research emphasis was on the reaction products after the formation of CH_3NO . The most noteworthy products were HCN , OH , and HNO_3 . Their reaction mechanism is shown below:

- 1) $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}$
- 2) $\text{I} + \text{I} + \text{M} \rightarrow \text{I}_2 + \text{M}$
- 3) $\text{CH}_3 + \text{NO} + \text{M} \rightarrow \text{CH}_3\text{NO} + \text{M}$
- 4) $2\text{CH}_3\text{NO} \rightarrow (\text{CH}_3\text{NO})_2$
- 5) $\text{CH}_3\text{NO} + \text{NO} \rightleftharpoons \text{CH}_3(\text{NO})_2$
- 6) $\text{CH}_3(\text{NO})_2 + \text{NO} \rightarrow \text{CH}_3 + \text{N}_2 + \text{NO}_3$
- 7) $\text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2$
- 8) $\text{NO}_2 + \text{CH}_3 + \text{M} \rightarrow \text{CH}_3\text{NO}_2 + \text{M}$
- 9) $\text{NO}_2 + \text{CH}_3\text{NO} \rightarrow \text{CH}_3\text{NO}_2 + \text{NO}$
- 10) $\text{CH}_3\text{NO} \rightarrow \text{CH}_2\text{NOH}$
- 11) $\text{CH}_2\text{NOH} \rightarrow \text{HCN} + \text{H}_2\text{O}$
- 12) $\text{CH}_2\text{NOH} + \text{NO} + h\nu \rightarrow \text{HCN} + \text{HNO}_2 + \text{H}$
- 13) $\text{H} + \text{HX} \rightarrow \text{H}_2 + \text{X}$
- 14) $\text{H} + \text{NO} + \text{M} \rightarrow \text{HNO} + \text{M}$

The fact that hydrogen cyanide and nitric acid have been identified as reaction products of $\text{CH}_3\text{I} + \text{NO}$ mixtures is not significant when one realizes that the total pressure in the reaction chamber did not exceed three torr. These conditions do not exist in the environment.

In summary, the continuous absorption of gaseous methyl iodide in the wavelength region around 2500Å indicated that the primary quantum yield of the dissociation $\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}$ was unity, but the quantum yields of the decomposition products, mainly methane, ethane, and iodine are very small. This low quantum yield is attributed to the back reactions reforming methyl iodide. Increasing sensitivity of analytical techniques has enabled workers to show that the photooxidation of methyl iodide is complicated and a large number of reactions occur.

The forward reaction is accelerated by the presence of silver which reacts with atomic or molecular iodine and by the presence of oxygen and nitric oxide which react with methyl radicals. A striking feature of the photodecomposition of methyl iodide was the discovery that the reaction $\text{CH}_3 + \text{CH}_3\text{I} \rightarrow \text{CH}_4 + \text{CH}_2\text{I}$ would require an activation energy of 8-9 kcal/mole for it to make an appreciable contribution to the overall reaction at room temperature. The "hot" methyl radical theory was propagated to explain these results. The energy of the absorbed photon at 2537Å is greatly in excess of the $\text{H}_3\text{C} - \text{I}$ bond dissociation energy.

3.3.3 Ambient Measurements -

CH₃I has been measured in the ambient air by Lovelock as mentioned earlier, at a mean background level of 0.001 ppb. However, some serious question concerning experiment artefacts in the analytical technique have been raised by Wilkness et al.⁽¹³⁾. The implication of this possibility to some of our measurements will be commented upon in a later section (6.2.2) of this report.

3.4 Carbon Tetrachloride

3.4.1 Sources, Uses, Toxicity-

Carbon tetrachloride is an excellent solvent. It is volatile and, when present in high concentrations, has a narcotic effect on the central nervous system⁽⁵⁵⁾. Carbon tetrachloride is a clear, colorless, sweet smelling liquid which had been used as an anesthetic, anthelmintic, and as a hair shampoo⁽⁵⁶⁾. These uses have been discontinued and the greatest use of carbon tetrachloride today is in industrial applications: metal degreasing; solvent for rubber cement and paints; fumigant for grain; dry cleaning agent; manufacturing intermediate for soap, chloroform, dyes, insecticides, plastics, inks, and freon gases; and as a fire extinguishing agent⁽⁵⁶⁾. In the 1930's, carbon tetrachloride displaced naphtha as the premier dry cleaning agent due to its non-flammability. It was soon displaced by tetrachloroethylene for its lower toxicity.

One of the major uses of carbon tetrachloride has been as a fire extinguisher. It appeared with the advent of electrical machinery since it is non-conductive. Carbon tetrachloride fire extinguishers were found to inhibit fires of flammable liquids. Injuries had been reported where workers were overcome by carbon tetrachloride vapors and a by-product produced when carbon tetrachloride is exposed to high temperatures, phosgene gas.

Carbon tetrachloride is an extremely toxic substance, capable of causing extensive damage to the liver, kidneys, lungs, and the heart. The three modes of exposure are ingestion, inhalation, and absorption through the skin and mucous membranes. The most frequent route of exposure appears to be by inhalation. Carbon tetrachloride poisoning causes necrosis in both the liver and kidney. The kidney damage results in destruction of cells whose function, in part, is to eliminate toxins from the blood. A major function of the liver is also to detoxify the blood. When carbon tetrachloride poisoning is severe enough to cause kidney and liver damage, the body's exposure to this poison is thus prolonged, which compounds its toxic effect to the rest of the body.

As an example of how small an amount of carbon tetrachloride can produce dangerous concentrations, one teaspoonful of carbon tetrachloride placed in an unventilated bathroom 6' by 10' by 8' would vaporize and produce a concentration of 100 ppm. The threshold limit value of carbon tetrachloride set by the American Conference of Governmental Industrial

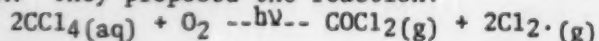
Hygienists is 5 ppm. It is for this reason that the Federal Government has banned its use in the home as a hazardous substance⁽⁵⁷⁾.

The total sum of carbon tetrachloride in the atmosphere greatly exceeds that which is accounted for by global production figures. It was therefore postulated by Lovelock et al.⁽⁴⁰⁾ and later confirmed by Singh et al.⁽⁴⁾ that a natural source exists for carbon tetrachloride in the atmosphere. Lovelock⁽⁴⁰⁾ states that carbon tetrachloride could be formed by reaction of chlorine with methane in the troposphere. Carbon tetrachloride has been experimentally observed by us⁽⁴⁾ during the simulated tropospheric irradiations of standard mixtures of perchloroethylene in air as will be discussed later in this report (Section 7.2). It is even possible that tropospheric reactions of other chlorinated olefins would result in the formation of carbon tetrachloride in the troposphere.

3.4.2 Reactivity Studies -

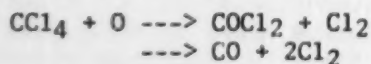
The reactions of carbon tetrachloride have been thoroughly investigated in the literature. Its photochemical reactions, however, are less well understood.

In 1935, Lyons et al.⁽⁵⁸⁾ photo-oxidized liquid carbon tetrachloride at 2537Å. They proposed the reaction:

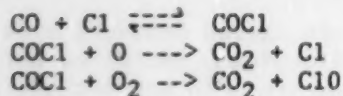


This reaction only occurs with the exclusion of water and it does not react in the absence of oxygen. The appearance of phosgene is significant in that phosgene has been used as a nerve gas and as a vesicant in chemical warfare.

In 1961, Ung and Schiff⁽⁵⁹⁾ reacted oxygen atoms with carbon tetrachloride vapor. Their primary reactions were bimolecular:



No other products were reported except for carbon dioxide which could be produced by the chain sequence:



The rate constant for the primary process was found to be independent of atomic oxygen, molecular oxygen and carbon tetrachloride concentration:

$$K = 3.3 \times 10^{-14} \exp \frac{-4500}{RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}.$$

This could lead to a carbon tetrachloride half-life of 4600 years at the ambient levels of atomic oxygen in the troposphere.

Carbon tetrachloride has been used as an intermediate for the manufacture of many industrial chemicals. Hexachloroethane is formed when CCl_4 and alcohol are reacted in ultraviolet light⁽⁶⁰⁾. The byproducts of this reaction are hydrochloric acid, chloroform, and various aldehydes. Styrene and vinyl butyl ether are photopolymerized in the presence of carbon tetrachloride⁽⁶¹⁾ at 3660Å and 3080Å. These processes occur under controlled conditions of temperature and pressure that are not present in the troposphere.

Carbon tetrachloride was photolyzed and reacted with ethane and ethylene at 2537Å by Roquette and Wijnen⁽⁶²⁾. the primary step produces trichloromethyl radicals and chlorine atoms. Although only 1% of the carbon tetrachloride originally present was decomposed, this reaction could have serious consequences in the stratosphere where radiation below 2900Å is not filtered by the ozone layer⁽⁶³⁾.

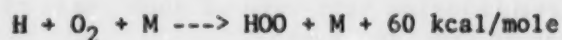
The following reaction mechanism was suggested to explain the formation and recombination of the products from the photo-initiated reaction with ethane:

- 1) $\text{CH}_2\text{Cl}_2 + h\nu \rightarrow \text{CCl}_3 + \text{Cl}$
- 2) $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5\text{Cl}$
- 3) $2\text{C}_2\text{H}_5\text{Cl} \rightarrow (\text{C}_2\text{H}_5\text{Cl})_2$
- 4) $2\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4\text{Cl}_2$
- 5) $2\text{C}_2\text{H}_5\text{Cl} \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_3\text{Cl}$
- 6) $2\text{CCl}_3 \rightarrow \text{C}_2\text{Cl}_6$
- 7) $\text{C}_2\text{H}_5\text{Cl} + \text{CCl}_3 \rightarrow \text{CCl}_3\text{C}_2\text{H}_5\text{Cl}$
- 8) $\text{C}_2\text{H}_5\text{Cl} + \text{CCl}_3 \rightarrow \text{CCl}_3\text{H} + \text{C}_2\text{H}_3\text{Cl}$

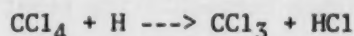
The reaction mechanism for the reaction with ethylene is very similar to 1-8 and the rate constants are usually faster due to the lower activation energies of the ethyl radical.

Tomkinson et al.⁽⁶⁴⁾ decomposed carbon tetrachloride at 2537Å but not at 3130Å. This study of the abstraction of chlorine atoms by methyl radicals was made at high temperature (90 - 140°F). Since the source of methyl radicals was a thermal decomposition of di-t-butylperoxide, errors can be introduced in the determination of the reaction rates and especially in trying to extrapolate the data to ambient conditions.

Clark and Tedder⁽⁶⁵⁾ reacted hydrogen atoms with carbon tetrachloride and generated the products: hydrogen chloride, chloroform, methylene dichloride and methyl chloride. The experimental apparatus did not include a device for measuring hydrogen atoms from the discharge of a Wood's tube, but the author's estimate the concentrations of the reactants to discover the reaction mechanism. The hydrogen atoms produced in the troposphere (from the photolysis of formaldehyde) react rapidly with oxygen to form hydroperoxyl radicals⁽⁴²⁾.



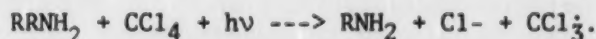
It is unlikely then, that the hydrogen abstraction reaction:



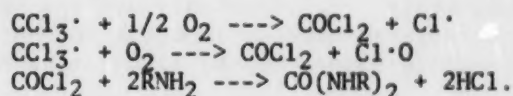
would be significant in the environment.

In 1968, Lautenberger et al.⁽⁶⁶⁾ photochemically reacted n-butylamine with liquid carbon tetrachloride. The products were mainly chloroform, hexachloroethane and ammonia. Approximately 90% of the light was at 2537Å and the reaction cell was maintained at room temperature.

Both ionic and free radical mechanisms have been proposed to explain their experimental results but the conclusion of the authors is that a free radical chain reaction is initiated by the absorption of light by the charge-transfer complex of the amine with carbon tetrachloride:



In the presence of oxygen, chloroform and hexachloroethane yields are reduced. The trichloromethyl radicals ($\text{CCl}_3^\cdot$) react with oxygen to yield phosgene which then reacts quickly with excess amine to form urea.



These photochemical reactions in which carbon tetrachloride vapor is decomposed preclude reactions in which carbon tetrachloride could participate in the ambient atmosphere. Experiments were conducted to ascertain the possibility of any tropospheric sinks for carbon tetrachloride with special emphasis on nitrogen oxides, free radical hydrocarbons, ozone and atomic oxygen.

3.4.3 Ambient Measurements -

Carbon tetrachloride has been found in measurable amounts wherever and whenever it has been sought. Lovelock⁽¹⁹⁾ reported the mean aerial concentration over the Atlantic Ocean at 0.071 ppb. Simmonds et al.⁽¹⁶⁾ reported CCl_4 in the range 0.1-1.63 ppb. during a three-day study in the Los Angeles Basin. We have reported urban levels of about 0.17 ppb. in New Brunswick, N.J.⁽¹⁴⁾ and 0.19 ppb. in Bayonne, N.J.⁽⁵⁾. Lovelock⁽¹⁹⁾ has recently reported "background" concentrations of 0.11 and 0.14 ppb. in Western Ireland and over the North Atlantic respectively. He also gave data for CCl_4 concentrations as a function of altitude over central England which showed values of about 0.07 ppb. at 10 km. - i.e. above the tropopause.

3.5 1:1:1 Trichloroethylene

3.5.1 Sources, Uses and Toxicity -

Methyl chloroform has become an increasingly popular solvent in recent

years due to its low toxicity. It has been used primarily for metal degreasing but it has been promoted as a carbon tetrachloride substitute for use as an intermediate.

1,1,1-trichloroethane is a colorless liquid possessing a chloroform-like odor. It is not flammable and has been used in hairsprays, dry cleaning and as an aerosol propellant in combination with freons. The principal toxic action is the depression of the central nervous system. Below the current threshold limit value of 500 ppm, no physiological effects have been observed. Above that concentration, 1,1,1-trichloroethane has been used as an anesthetic. This is not a unique property of methyl chloroform, but one common to most chlorinated aliphatic hydrocarbon solvents.

1,1,1-trichloroethane has also been used as a degreening agent for produce such as tomatoes, berries, apples and citrus fruits. This application produces a deep, even coloration characteristic of normal ripe fruit and it effectively retards decay due to mold and fungus growth⁽⁶⁷⁾. For this specific agricultural application, methyl chloroform has been exempted from the requirement of a tolerance level for residues⁽⁶⁸⁾.

Experiments with humans exposed to 1,1,1-trichloroethane vapor show that most of the compound is exhaled immediately. 1,1,1-trichloroethane vapor, in high concentrations (>900 ppm), acts as an anesthetic agent and has only a slight capacity to cause reversible injury to the liver or kidneys⁽⁶⁹⁾.

3.5.2 Reactivity Studies -

There is a dearth of literature concerning the photochemical reactivity of 1,1,1-trichloroethane. It does not absorb in the visible or ultraviolet range. The C-C bond dissociation energy for 1,1,1-trichloroethane is 84.2 kcal/mole based on the heats of formation of chlorinated methyl radicals⁽⁷⁰⁾. This amount of energy is much too high to achieve any lysis of the bonds in the troposphere.

A study of chlorine-photosensitized oxidations of chloroethanes at 4360Å was conducted in 1971⁽⁷¹⁾. A concentration of 60 torr of 1,1,1-trichloroethane was irradiated with chlorine and oxygen at 355°K --- no products were formed. The authors explained this on the basis of the extreme exothermicity of the dissociation of the hypothetical radicals involved.

This compound seems to be tropospherically inert. The low solubility of 1,1,1-trichloroethane suggests that the ocean is not a sink. It may remain in the ecosphere as residue or more likely flux into the stratosphere.

3.5.3 Ambient Measurements -

Like CCl_4 , CH_3CCl_3 is considered to be ubiquitous and is generally found at sub-ppb levels. Simmonds et al.⁽¹⁶⁾ reported CH_3CCl_3 levels of 0.01 to 2.3 ppb during their 1974 study in the Los Angeles area. Lillian and co-workers' values for New Brunswick⁽¹¹⁾ and Bayonne, New Jersey⁽⁵⁾ were

respectively of 0.27 and 0.83 ppb. Lovelock's⁽¹⁹⁾ "background" concentrations were 0.065 and 0.075 ppb in western Ireland and over the Atlantic.

3.6 Trichloroethylene

3.6.1 Uses, Production and Toxicity -

Trichloroethylene is widely used in industry as a solvent particularly in the vapor degreasing of fabricated metals where 95% of that produced is utilized. In addition, TCE is used as an extraction solvent, a chemical intermediate and an anesthetic.

A common and simple technique for the production of trichloroethylene is through the use of acetylene as the raw material, but in recent years ethylene has been used instead due to its lower cost. For the most part, two methods are employed for the production of TCE from ethylene. One is photochlorination of 1,2 dichloroethane followed by dehydrochlorination of tetrachloroethane. The second technique involves oxychlorination of ethylene or dichloroethylene at high temperatures.

The demand for the production of TCE has been kept active mainly due to its use in the aircraft and space industries as well as other metal industries. The market was hurt in 1966 by a report by the Los Angeles County Air Pollution Control District which claimed that TCE was a significant pollutant contributing to the formation of photochemical smog⁽⁷²⁾. Since then, several private studies⁽²¹⁾ were undertaken which tended to downgrade its role in smog formation and restored some confidence in its use. The future of TCE in industry is as of now highly uncertain. The graph of sales of TCE (Figure 1) compiled from U.S. Tariff Commission reports on Synthetic Organic Chemicals tends to substantiate the uncertainty of TCE's future role in industry. Since 1970 the production of TCE has dropped some 29%.

The major physiological responses which result from exposure to trichloroethylene is one of central nervous system depression. Symptoms of acute exposure may include nausea, mental confusion and fatigue. Several fatalities have occurred due to severe acute exposure. These have been attributed to ventricular fibrillation resulting in cardiac failure. Also possible effects to liver metabolism are suspected. In a recent study by the National Cancer Institute⁽⁷³⁾, trichloroethylene has been found to cause cancer in mice. The evidence submitted is being questioned by producers of TCE due to the large doses given the mice and the means by which it was given (ingestion) which isn't the principal mode by which it is transferred to humans. Due to this evidence, an alert has been issued.

The toxic hazard ratings of trichloroethylene compiled by Sax⁽⁷⁴⁾ is as follows:

Acute local -

Irritant - slight
Ingestion - slight

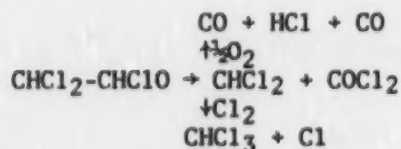
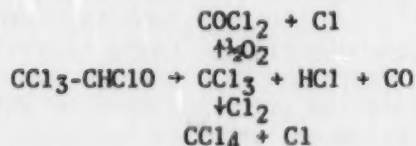
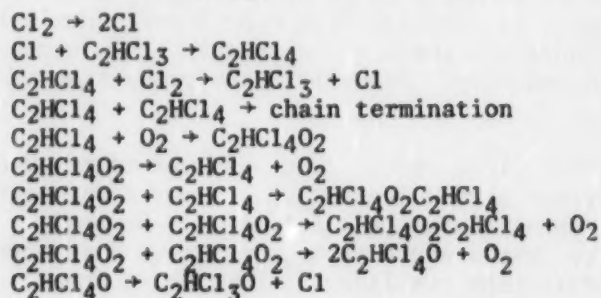
	Inhalation - slight
Acute systematic -	Ingestion - moderate Inhalation - high Skin absorption - moderate
Chronic local -	Irritant - slight
Chronic systematic -	Inhalation - slight Skin absorption - slight

Due to the above hazard rating and other information not mentioned, a TLV of 100 ppm has been set for trichloroethylene in the industrial environment.

3.6.2 Reactivity Studies -

There seems to be no doubt that trichloroethylene is a photochemically reactive compound. Several investigators have conducted studies on the compound utilizing different conditions yielding different results. Several of these studies will be discussed in this section.

Huybrechts and Meyers⁽⁷⁵⁾ studied the chlorine photosensitized oxidation of the compound at 363° and 403°K. They found that, depending on the temperature, between 82 and 90% of the compound was oxidized to dichloroacetyl chloride. Other products observed to form included chloroform, phosgene, carbon tetrachloride, carbon monoxide, HCl and trichloroethylene epoxide. The mechanism they proposed to explain this is as follows:



In addition, Huybrechts and Meyers⁽⁷⁶⁾ studied the oxygen effect in the photochlorination and found that oxygen tended to inhibit the reaction. They determined that the greater the O_2/Cl ratio the smaller the extent of photochlorination and the favored reaction is the oxidation.

Mayo and Honda⁽⁷⁷⁾ studied the autooxidation of trichloroethylene in the liquid phase and obtained results similar to Huybrechts, with the differences being accounted for by the fact that they didn't work in the gas phase.

Smog studies concerning trichloroethylene were conducted by Katherine Wilson⁽²⁴⁾ after the Los Angeles Air Pollution Control District first implicated TCE as a significant contributor to photochemical smog and producers became alarmed. In the study she found that TCE was not as significant as the Los Angeles team suspected. She concluded that if the ambient concentration didn't climb significantly upwards, no problem would result from TCE as far as smog is concerned. The conclusion was supported by experiments in which higher concentrations than those found in ambient air were used. The photoreactivity was found to be negligible. In a smog forming atmosphere, the presence of TCE didn't significantly increase eye irritation; and under conditions similar to those when pollutants leave an industrial stack (100 ppm), no increase in oxidant level was detectable.

Bufalini et al.⁽⁷⁸⁾ conducted experiments which showed phosgene as a product as well as traces of formyl chloride. Other products noted to form included HCl, carbon monoxide, HCOOH and nitric acid. The initial reactants in this irradiation were trichloroethylene and NO_2 .

3.6.3 Ambient Measurements -

Ambient measurements of TCE made by various investigators have documented its presence in both air and surface waters. Murray and Riley⁽¹⁴⁾ recorded concentrations of TCE in Great Britain and over the northeast Atlantic Ocean. The concentrations recorded varied significantly from one site to the next. At rural stations the values varied from 2 - 28 ng/m³; in the city of Liverpool the value reported was 850 ng/m³; over the northeast Atlantic detected concentrations varied from 1 - 22 ng/m³; and the surface waters analyzed contained from 5 - 11 ng TCE per liter. Lovelock⁽¹⁹⁾ monitored for trichloroethylene over the north Atlantic and western Ireland. The mean concentrations reported were 15 parts per 10¹² volume and less than 5 parts per 10¹², respectively. Lillian et al.⁽³⁸⁾ reported maximum and minimum values of TCE in the northeast United States from Baltimore, Maryland to Whiteface Mountain, New York. The mean values recorded at the different sites varied from highs of .92 ppb and .71 ppb in Bayonne, New Jersey and New York City, New York, respectively; and lows of less than .05 and .1 ppb in Baltimore, Maryland and Whiteface Mountain, New York, respectively.

3.7 Ethylene Dichloride

3.7.1 Uses, Production and Toxicity -

Approximately 75% of all the ethylene dichloride produced in the U.S. goes into the production of the vinyl chloride monomer; 7% is used as a chlorinated solvent intermediate such as in the production of trichloroethylene, and 5% is used as a lead scavenger. Other than the above, ethylene dichloride is used as an industrial solvent in cleaning and extraction processes, as a fumigant and as an anti-knock additive to gasoline.

Ethylene dichloride is produced by the addition of ethylene and chlorine. The techniques which are used in industry to carry out this reaction are as follows: (1) A reaction of ethylene and chlorine in a body of ethylene dichloride in a stirred tank reactor, or (2) the contact of ethylene and chlorine gases with a circulation stream of ethylene dichloride in a packed or empty reactor.

The demand for production of ethylene dichloride in industry has increased sharply since the mid 1960's as can be seen from the plot of sales compiled from U.S. Tariff Commission Reports (Figure 1). This increase is largely attributed to its role in the production of the vinyl chloride monomer and its increased use in the manufacturing of chlorinated solvents. As a solvent it has been displaced by trichloroethylene and CCl_4 . Due to increasing concern over the vinyl chloride monomer's role as a carcinogen, one cannot accurately predict future trends.

Physiological responses which result from exposure to high concentrations of ethylene dichloride are effects on the eyes, upper respiratory tract and the nose. In addition, liver, kidney and adrenal injuries may occur. Symptoms of acute exposure include irritation to the eyes, nose and upper respiratory tract, gastrointestinal upset, mental confusion, nausea and dizziness.

The toxic hazard ratings compiled by Sax⁽⁷⁴⁾ is as follows:

Acute local	Irritant - high (may cause permanent damage) Ingestion - high Inhalation - high
Acute systematic -	Ingestion - high Inhalation - high
Chronic local -	Irritant - moderate (reversible and irreversible changes, not severe)
Chronic systematic	-Ingestion - high Inhalation - high Skin absorption - moderate

At present the TLV for ethylene dichloride is set at 100 ppm but due to

the information available at the present time the A.C.G.I.H. has recommended a lowering of the TLV to 50 ppm⁽³⁷⁾.

3.7.2 Reactivity Studies -

Ethylene dichloride does not absorb wavelengths above 2900Å. No instances of its photochemical reactivity in air in this region of the spectrum have been found in the literature.

3.7.3 Ambient measurements -

As far as is known, no ambient measurements of ethylene dichloride have been reported.

3.8 Vinyl Chloride

3.8.1 Sources, Uses and Toxicity -

Vinyl chloride (monochloroethylene) is made by oxychlorination of ethylene or by hydrochlorination of acetylene. It boils at -13.9°C, and at room temperature is a colorless, faintly sweet-smelling gas. As a gas it is flammable and explosive, but is usually handled as a liquid under pressure. It has been used as a propellant for aerosol products.

Vinyl chloride is the parent compound of a series of thermoplastic resin polymers and copolymers which find wide use in containers, wrapping such as for food packing materials, film, electrical insulation, water pipes, conduit, and a variety of other industrial and consumer products. In the United States vinyl chloride has been made commercially since 1939. The vinyl chloride industry is divided into three segments: monomer production, polymer production, and fabrication. Vinyl chloride (VC) is used primarily in the production of polyvinyl chloride (PVC), a resin which is produced through batch processing.

The vinyl chloride/polyvinyl chloride industry is a multi-billion dollar concern involving several dozen large manufacturers of vinyl chloride and polyvinyl chloride resin and thousands of fabricators producing a variety of products based on polyvinyl chloride and probably employing more than 300,000 workers. The production of vinyl chloride from 1969 to 1974 rose at an average annual growth rate of 14%. In 1975 output dropped from a 1974 level of 5.60 billion lb. to 4.20 billion lb., a 25.4% drop in production. An increase in output above 1975 levels is predicted for 1976. Because of the renewed increased consumption of polyvinyl chloride, the lack of new production capacity and the effect of regulations on vinyl chloride emissions, there may be a production shortage by 1977.

Prior to January 1974, vinyl chloride had been regarded as having moderate liver toxicity. Patty⁽⁷⁹⁾ stated that the dominant handling problem was the fire and explosion hazard. On January 22, 1974, the Occupational Safety and Health Administration (OSHA) was informed by the National Institute for Occupational Safety and Health (NIOSH) that the B.F. Goodrich Chemical Company, the largest U.S. producer of PVC resin, reported

that deaths of several of its employees from a rare liver cancer (antio-sarcoma) may have been occupationally related. A joint inspection of the B.F. Goodrich plant by State and Federal agencies followed soon after, and on February 15, 1974, a fact-finding hearing was held.

The investigating groups (in the United States and Europe) looking into the circumstances of VC and PVC production began one of the most urgent medical inquiries in history. In the United States they included: (1) the Occupational Safety and Health Administration (OSHA) of the Department of Labor; (2) the National Institute for Occupational Safety and Health (NIOSH); (3) the Environmental Protection Agency (EPA); (4) the Center for Disease Control (CDC); (5) the National Institute of Health (NIH); (6) the American Cancer Society (ACS); (7) the Environmental Science Laboratory, Mount Sinai School of Medicine, New York; plus some industrial investigations, in particular those undertaken by the Manufacturing Chemists Association (MCA).

In 1975, vinyl chloride production in the United States was 4.20 billion lbs. The estimated loss of vinyl chloride during processing is approximately 3.0 - 6.3% and the polyvinyl chloride loss is of the order of 1.3% at the PVC polymerization facilities, with more than 75% of the losses being vinyl chloride air emissions⁽⁸⁰⁾. Thus, in the United States alone, substantial amounts of vinyl chloride (in 1975 probably exceeding 120 million lbs.) and large quantities of polyvinyl chloride (probably exceeding 50 million lbs.) were discharged into the environment during the PVC polymerization production processes. Most of the vinyl chloride escapes directly into the atmosphere, with lesser amounts dissolved in water effluent streams and entrapped in sludge and solid wastes. The polyvinyl chloride losses occur as particulates in air emissions, suspended solids in water effluents, and components of solid wastes.

The principal source of vinyl chloride leakage is in the operation of the polymerization kettles. Other losses occur during the transfer of vinyl chloride from tank cars to storage areas, during the PVC drying process and from a variety of valves, flanges and pump seals. Dust collector losses and disposal of oversize particles are some of the areas accounting for polymer losses.

Another area of potential vinyl chloride exposure concerns the presence of the unreacted monomer entrapped in polyvinyl chloride products. The existence of residual vinyl chloride in articles made from vinyl chloride polymers is related to the manufacturing process and the physical structure of the polymers. In early March 1975, Professor Cesare Maltoni disclosed that vinyl chloride caused cancer when fed to rats⁽⁸¹⁾. These results put vinyl chloride in conflict with the "Delaney" clause. This states that any substance that causes cancer in even one animal must be banned from contact with food or cosmetic products.

On September 3, 1975, the U.S.F.D.A. proposed regulations to restrict the uses of vinyl chloride polymers in contact with food⁽⁸²⁾ by banning rigid and semirigid polyvinyl chloride articles intended to contact food,

including bottles, blister packs, boxes and pipe. The use of PVC in coatings applied to fresh citrus fruits would also be prohibited⁽⁸³⁾. The continued use of PVC in food contact items such as films, gaskets, capliners, flexible tubing, and package coatings would be permitted by FDA. The use of water pipes made from PVC would also be allowed, subject to provisions concerning an interim food additive regulation.

Until recently, levels of unreacted vinyl chloride entrapped in PVC products were estimated between 50 and 1000 ppm⁽⁸⁰⁾. The new methods of making PVC are aimed primarily at reducing worker exposure to vinyl chloride as required by OSHA. According to the Society of the Plastics Industry, the residual level of vinyl chloride in certain resins is now less than 1 ppm⁽⁸⁴⁾, and due to improved manufacturing methods, for all practical purposes, no vinyl chloride can migrate to food⁽⁸⁵⁾.

The production of PVC bottles accounts for only 8% of the total plastic bottle market. Anticipation of federal regulations has led some PVC makers to shift away from PVC bottles for food products⁽⁸⁶⁾. Packagers have been concerned about the safety of PVC bottles since the FDA discovered in 1973 that vinyl chloride leaked into distilled alcoholic beverages contained in PVC bottles⁽⁸²⁾.

Vinyl chloride has been used as an aerosol propellant in a variety of products, including hair sprays. Although the precise data when vinyl chloride was first used for this purpose is uncertain, as far back as 1959, a review on the use of CH_2CHCl and CH_2Cl_2 as propellants in aerosols was published⁽⁸⁷⁾. At one time, vinyl chloride was one of the most commonly used propellants in aerosol products⁽⁸⁸⁾. A list of over 50 different pesticidal sprays containing vinyl chloride including many used indoors has been compiled by EPA⁽⁸⁰⁾.

A 1964 report estimated that an aerosol product sprayed in a tiny room of 282.5 ft³ for 30 sec. would result in 0.025% (or 250 ppm) vinyl chloride by volume⁽⁸⁸⁾. It might be noted here that Dr. Cesare Maltoni reported, in early 1975, on the development of angiosarcoma of the liver in test animals at vinyl chloride levels as low as 50 ppm⁽⁸⁹⁾.

In April 1974, FDA asked for recalls of hairsprays containing vinyl chloride made by two major producers. Other manufacturers were requested to recall any outstanding stocks of such products from the market. EPA had earlier asked makers of 23 insecticide sprays containing vinyl chloride to reformulate their products⁽⁹⁰⁾. The use of vinyl chloride as a propellant in cosmetic aerosols was prohibited in a final regulation⁽⁹¹⁾. A new drug application for the marketing of aerosol drugs containing vinyl chloride as a propellant was also required.

The EPA banned the use of vinyl chloride as a propellant in certain pesticide aerosols in April 1974⁽⁹²⁾ and the Consumer Product Safety Commission banned the use of other self-pressurized household products containing vinyl chloride in August 1974⁽⁹³⁾.

As results of the various toxicity studies of vinyl chloride became known, the mounting evidence pointed to this chemical as the main agent responsible for the induction of liver angiosarcoma. Much of the early toxicity studies were conducted by Professor Cesare Maltoni, Instituto Di Oncologia, Bologna, Italy, and by Dr. P.L. Viola of the University of Rome. In 1970 almost four years before the discovery at the B.F. Goodrich plant, Dr. Viola produced tumors in the bones, skin and lungs of rats exposed to 30,000 ppm (3%) of vinyl chloride⁽⁹⁴⁾. In 1971, Dr. Maltoni began to test animals at lower concentrations of the gas.

His investigations involved various types and levels of exposure to vinyl chloride. At the New York Academy of Sciences meeting, May 10-11, 1974, he reported the development of angiosarcoma of the liver and other types of tumors at levels of atmospheric exposure as low as 50 ppm⁽⁸⁹⁾.

Vinyl chloride has also been linked to other health-related effects. Considerable data exists concerning the toxic effects of vinyl chloride from atmospheric exposures, especially by inhalation and occupational contact. There is ample evidence that vinyl chloride inhalation can result in acute toxicity manifested by an array of symptoms including unconsciousness. Vinyl chloride has been implicated as a causative agent for acroosteolysis of the hands and feet as well as systemic effects among workers engaged in the manufacture of vinyl chloride. In one report, approximately 1-3% of the workers involved in the manual cleaning of PVC reactor vessels had at one time experienced acroosteolysis⁽⁸⁰⁾. It is characterized by a soreness and thickening of skin at fingertips, gradual dissolution of bone calcium at the fingertips and toes, skin sores, and frequently heightened sensitivity of hands to cold. These symptoms occur only after several years of high levels of exposure.

A number of chemical companies, in early 1974, just after the B.F. Goodrich disclosure, stated that they had not been in violation of the federal standard for exposure to vinyl chloride vapors. The Treshold Limit Value or TLV had been set at 500 ppm, in April 1959, by the A.C.G.I.H. Dow Chemical, a major vinyl chloride maker, as early as 1961, had urged use of a 50 ppm exposure level⁽⁹⁵⁾. Studies in 1961 on the chronic effects of vinyl chloride on laboratory animals⁽⁹⁶⁾ indicated some effects at 100-200 ppm and 100 ppm was suggested as a T.L.V.

Partly because of toxicity studies of vinyl chloride implicating it as the causative agent in the induction of angiosarcoma of the liver, and because employees were being exposed at levels around the experimentally observed effect level of 250 ppm, an Emergency Temporary Standard (ETS) was promulgated by OSHA on April 5, 1974⁽⁹⁷⁾. This standard reduced the level from a ceiling of 500 ppm to 50 ppm.

Additional vinyl chloride toxicity studies by the Industrial Bio-Test Laboratories, Northbrook, Illinois revealed that mice exposed to 50 ppm vinyl chloride for 7 months developed angiosarcoma of the liver. On May 10, 1974 OSHA proposed a permanent standard for employee exposure at

no detectable level, as determined by a sampling and analytical method capable of detecting vinyl chloride at concentrations of 1 ppm with an accuracy of 1 ppm $\pm$ 50%. Engineering controls and work practice programs were also required to reduce levels below detectability. On October 4, 1974 the new federal standard was published in the Federal Register and became effective on April 1, 1975⁽⁹⁸⁾. The standard required that exposure to vinyl chloride not exceed 1 ppm averaged over an 8-hour period and 5 ppm averaged over a 15-minute period.

3.8.2 Reactivity Studies -

Because of the interest in occupational exposures to vinyl chloride, there have been several recent studies on various aspects of its photooxidation. Sanhueza et al.⁽⁹⁹⁾ have studied the chlorine-atom and O(³P)-initiated oxidations of this compound. Gay et al.⁽⁷⁸⁾ have also investigated vinyl chloride as part of an overall study of chlorinated ethylenes. Here, vinyl chloride was U.V.-photooxidized in air in the presence of NO₂. Ozonolysis was also studied to help elucidate the contribution of this process to the reaction mechanism. Huie et al.⁽¹⁰⁰⁾ investigated the kinetics of the reaction of O(³P) with several haloethylenes including vinyl chloride. Arnold et al.⁽¹⁰¹⁾ have examined chemiluminescence from the reaction of oxygen atoms and vinyl chloride. Rennert⁽¹⁰²⁾ studied vinyl chloride photolysis in presence of radical scavengers (I₂, H₁, H₂S) in presence of added inert gases. Williamson and Cvetanovic⁽¹⁰³⁾ have measured reaction rates of ozone with chlorinated olefins in CCl₄ solution. Ozone attack was found to be electrophilic, decreasing in rate as the number of chlorine atoms in the molecule increased.

All these studies show that vinyl chloride is reactive, though patterns of products and postulated reaction mechanisms vary, depending on the particular experimental conditions employed. Arnold et al.⁽¹⁰¹⁾ observed formaldehyde and many other products, and suggest a mechanism involving O-atom addition to the double bond, forming an intermediate which decomposes to an aldehyde and a carbene. Williamson and Cvetanovic⁽¹⁰³⁾ observed only phosgene as a product. Huie et al.⁽¹⁰⁰⁾ failed to detect formaldehyde as a product of O₃ reacting with vinyl chloride. They attributed this to reaction of the formaldehyde with O₃ to produce formic acid or CO and H₂O.

Gay et al.⁽⁷⁸⁾ have detected formaldehyde in other products. Formaldehyde was produced rapidly, rising to 0.85 ppm after 160 minutes. An ozonolysis study of vinyl chloride produced a maximum of 0.75 ppm formaldehyde. They also observed formation of HCl at levels about 50% higher than the formaldehyde. Formyl chloride was also a product, but being thermally unstable it rapidly decomposes to CO and HCl. Sanhueza and Heicklen⁽⁹⁹⁾ in a study of the O(³P)-initiated oxidation of vinyl chloride, also found evidence of formyl chloride production in the presence of oxygen.

Arnold et al.⁽¹⁰¹⁾ observed vibrationally excited HCl when vinyl chloride is introduced into a stream of O-atoms. This was attributed partly to thermal decay of formyl chloride, but predominantly by a reaction of hydrogen atoms with Cl₂ (another observed reaction product).

3.8.3 Ambient Measurements -

The EPA and other groups have made ambient measurements of vinyl chloride. Monitoring results from EPA at a number of industrial PVC and VC plants seem to indicate that the levels of vinyl chloride in ambient air near the plants fluctuate sharply.⁽⁸⁰⁾ Nearly all collected samples contained detectable levels of vinyl chloride, <1 ppm. A number of individual air samples contained >1 ppm. Water effluents were also monitored for vinyl chloride, and the levels varied considerably. The highest level was 20 ppm, with 2-3 ppm a more typical level. Grimsrud and Rasmussen⁽¹⁰⁴⁾ searched for vinyl chloride plus 18 other halocarbons in the atmosphere of the rural northwest (southeast Washington state). Vinyl chloride could not be detected, <5 ppt, using a GC-MS system.

3.9 Dichloromethane

3.9.1 Sources, Uses and Toxicity -

Of the more than 520 million pounds of dichloromethane produced during 1973, most of this was applied in uses requiring a very strong solvent. Dichloromethane, in addition to those uses already cited, is also used as a solvent for cellulose esters, for polyvinyl acetate, chloride and chloroacetate, methyl and ethyl cellulose, rubber, bitumen, pitch, oils, waxes and other resins⁽¹⁰⁵⁾. It is especially suitable as a solvent in the preparation of polycarbonates by phosgenation in the presence of pyridine⁽¹⁰⁶⁾. Dichloromethane is also finding increasing use instead of trichloroethylene in vapor degreasing of metal parts in industrial metal fabricating plants⁽¹⁰⁷⁾. This action stems from the recently reported liver carcinogenicity of TCE in mice. An additional use now just being realized for dichloromethane involves the use of CH₂Cl₂ instead of previously used TCE in the manufacture of some ground and instant decaffeinated coffees⁽¹⁰⁸⁾. According to the FDA, methylene chloride use in these processes is allowed since it continues on the approved list pending further studies. FDA has no information at present to indicate that CH₂Cl₂ poses any hazard.

Another important use of methylene chloride is as an aerosol propellant. Some reviews covering its manufacture, physical, physiological and chemical properties, and its use in aerosols have been published^(87,109). Cannizaro et al.⁽¹¹⁰⁾ resolved 18 volatile components of commercial aerosol formulations, consisting of mixtures of hydrocarbons, chlorinated and fluorinated hydrocarbons, and aliphatic halides. The properties and methods of preparation of CH₂Cl₂ in aerosol formulations has also been published by K. Bergwein⁽¹¹¹⁾.

The suitability of dichloromethane as an aerosol propellant is dependent upon a number of factors. These are: (1) vapor pressure between 15 - 100 psig at 70°F; (2) non-flammability; (3) freedom from odor; (4) chemical inertness to other materials in the formulation; (5) a low order of toxicity and (6) freedom from irritation⁽¹¹²⁾. While it is a good solvent, dichloromethane is also slightly irritating to the eyes when sprayed in the air. As a propellant, dichloromethane can be found in formulations such as shaving cream, dry shampoos, deodorants, hair cosmetics, pharmaceutical products, food aerosols and pesticides.

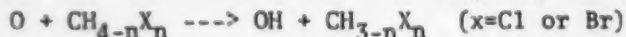
Other health effects of dichloromethane have been observed. Its vapor offers a definite industry hazard unless care is taken with ventilation. It is narcotic and toxic though not as much as chloroform which it closely resembles in its physiological effects. At high concentrations it is a rapid anesthetic and death may result from asphyxia. Its high vapor pressure at ordinary temperatures increases this hazard. Extreme care with ventilation and avoidance of skin contact is necessary where this solvent is used industrially. Long or repeated exposure to lower sub-narcotic concentrations may result in organic injury to liver, kidneys and other organs⁽¹¹³⁾.

The in-home use of paint removers containing dichloromethane results in the absorption of this solvent, which is metabolized to CO, and can eventually lead to heart stress⁽¹¹⁴⁾. In Sweden, human subjects were exposed for controlled periods to varying concentrations of dichloromethane, but no detrimental effects were observed. Methylene chloride has been an air pollutant problem in other areas also, ranging from air contamination of space vehicles to a hazard during welding operations⁽¹¹⁵⁾.

3.9.2 Reactivity Studies -

Some simulated atmospheric photodecomposition studies have been reported. Dilling et al.⁽¹¹⁶⁾ found that less than 5% of the initial dichloromethane had reacted in 21 hours in the presence of NO, and less than 5% in 7.5 hours in presence of NO₂. Sanhueza and Heicklen⁽⁹⁹⁾ studied the chlorine-atom sensitized oxidation of dichloromethane and chloromethane at 3655 Å and 32°. The initial major products were found to be CHClO and HCl, with smaller amounts of CCl₂O and CO being produced. The formation of CO resulted from the decomposition of CHClO, thus it was considered a secondary product.

Arnold et al.⁽¹¹⁷⁾ investigated the infrared chemiluminescence from the reactions of oxygen atoms with halomethanes. In these reactions, the chemiluminescence produced arose from vibrationally excited CO and HCl. Some other reaction products observed were CO₂, Cl₂, CCl₂O, C₂H₂Cl₂, C₂H₂Cl₂O, C₂H₂ and CH₄. It seems likely that the initial reaction steps are the abstraction of a hydrogen atom from the halomethane



followed rapidly by



Lin⁽¹¹⁸⁾ has observed in chemical laser studies that $O(^1D)$ atoms obtained from the U.V. photolysis of ozone readily insert into the C-H bonds of molecules such as CH_nX_{4-n} ($X=F, Cl$) and that the resulting unstable alcohol eliminates HX ($X=F, Cl$) producing vibrationally excited HF or HCl .

3.9.3 Ambient Measurements -

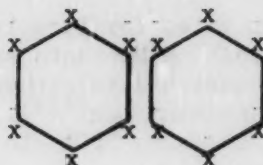
Some groups have attempted to measure CH_2Cl_2 in air and water. Grimsrud and Rasmussen⁽¹⁰⁴⁾ using a Durapak Carbowax 400/Porasil F column linked to an MS system, failed to detect CH_2Cl_2 in the northwest United States, $CH_2Cl_2 < 5$ ppt. The authors concluded that the detection of CH_2Cl_2 and CH_3Cl might increase further the relative role chlorocarbons play as the means of transporting chlorine to the stratosphere. The compound CH_3Cl however was detected at a level of about 530 ± 30 ppt. Dowty et al.⁽¹¹⁹⁾ detected CH_2Cl_2 and many other halogenated aliphatic compounds in water from a New Orleans water treatment plant.

3.10 Polychlorinated Biphenyls (PCBs)

3.10.1 Sources, Uses and Toxicity -

Polychlorinated biphenyls (PCBs) are one member of a group of industrial organochlorine compounds which have recently been recognized as a widespread, persistent contaminant in the environment. Since their introduction in 1929, PCBs have come into use as dielectric fluid in capacitors, insulating/cooling fluids in transformers, and high temperature and pressure lubricating fluids⁽¹²⁰⁾. However, it was not until 1966 that Jensen first identified PCBs in environmental samples⁽¹²¹⁾. The usually present "unknown interfering peaks" on gas chromatograms of DDT extracts were identified as PCBs. Following Jensen's discovery, many surveys of fish and birds were conducted revealing the ubiquity of this new contaminant⁽¹²²⁾. The potential hazard PCBs presented to human health was emphasized in 1968 by the sickening of more than 1000 persons in Japan who had used a cooking oil contaminated by PCBs. Again, in 1971, the U.S. Food and Drug Administration seized 75,000 eggs laid by chickens which had eaten PCB contaminated fish meal. In reaction to the opinion of the scientific community, Monsanto Chemical Company, the sole producer of PCBs in the U.S., voluntarily announced a restricted sales policy for PCBs⁽¹²³⁾. Beginning in 1971 Monsanto would sell only to closed system users and Monsanto would recycle or incinerate expended PCB containing material. Nevertheless PCBs are still being measured in air, water, sewage, and in human adipose tissue.

As evidenced by its structure, substitution of chlorine atoms onto the ten available sites of the biphenyl ring can produce many isomers.



Two hundred and ten combinations are possible but about 100 are thought to be probable considering reaction conditions and the unlikelihood of greatly unbalanced chlorination of the benzene rings⁽¹²⁴⁾.

Sissons and Welti used a combination of gas chromatography, NMR, and mass spectroscopy to examine the isomeric content of several commercial PCB mixtures⁽¹²⁵⁾. Identification of nearly all of the mixtures was accomplished. They found that Aroclors (Monsant's trademark for PCBs) of 42% chlorine content contained 45 isomers, those of 54% chlorine content contained 69 isomers and those of 60% content contained 78 isomers.

The appearance of the PCBs differ according to their chlorine content. Aroclors of 21 to 62% chlorine appear as colorless mobile oil to light yellow sticky resin⁽¹²⁶⁾. Aroclors of 68 and 70% chlorine are white and white crystalline powders respectively. The PCBs as a group and especially the higher chlorine content mixtures are extremely nonflammable. Coupled with their special dielectric properties, the PCBs have become invaluable in electrical application. The higher chlorinated compounds possess a very low vapor pressure. Most of the PCBs are soluble in organic solvents but not in water. Solubilities in water as stated by Monsanto are as follows: 42% chlorination - 200 ppb, 48% chlorination - 100 ppb, 51% chlorination - 50 ppb, and an estimated 25 ppb for 60% chlorination. In addition, the PCBs are extremely resistant to chemical attack. They are unaffected by moderate to rigorous attack by acids or bases; but PCBs will react with sodium hydroxide at elevated temperatures to form phenolic compounds. Lastly, Monsanto states that PCBs are resistant to mildew and microorganisms.

The chemical inertness of PCBs combined with their low volatility, flame resistance, high dielectric constant and their compatibility with chlorinated hydrocarbons find PCBs many specialized applications. Before Monsanto adopted its "closed system" use sales policy in September 1970, 60% of sales were for dielectric material in electrical capacitors and for insulating/cooling oils in large power transmission transformers⁽¹²⁷⁾. Another 25% of sales were for use as plasticizers, which included the incorporation of PCBs in polyvinylchloride for flexibility and also for use in producing carbonless reproducing paper, e.g. credit card receipts. Less than 5% of sales went for miscellaneous applications including: surface coatings, adhesives, printing ink and pesticide extenders.

As previously mentioned, Monsanto initiated a sales policy whereby they would phase out sales to customers of open system use and would continue to sell to users where the end product would be recycled or destroyed.

This amounted to reducing their sales for largely electrical capacitors and power transformers. (In addition Monsanto set up a system to collect fluids from closed system uses and to either regenerate or destroy PCBs through high temperature incineration⁽¹²⁷⁾.) By 1972 Monsanto expected to have reduced their sales to 100% closed system use.

Lastly Monsanto would move to discontinue the higher chlorinated biphenyls and move to biphenyls of 48% or less chlorine content. The lower chlorinated biphenyls would stand a better chance of microbial degradation in the environment as supported by some experimental results.

In addition to Monsanto, other companies outside the U.S. produce PCBs. Worldwide production figures are not available. However, the U.S. produced 33×10^6 Kg in 1970 while Japan produced an estimated 11×10^6 Kg⁽¹²¹⁾.

Japan's market was similar to the U.S.: 40-50% for capacitors, 15% for transformer oil, 10-15% for heat transfer fluid, 5% for plasticizers, 15% for carbonless reproducing paper, and 5-10% for export.

Foreign manufacturers of PCBs and their trade names include: Prodelec, France (Phenocolor); I.G. Farber Industrie A.G., Germany (Clophen); Kanegafuchi Chemical Company, Japan (Kannechlor); Mitsubishi - Monsanto, Japan (San-To therm); Caffaro, Italy (Fencior); and U.S.S.R. (Sovol)⁽¹²⁸⁾.

Of the estimated 45×10^7 Kg of PCBs produced in North America between 1930-1970 it has been reasoned that 78% was released to the environment; the balance of the material is either still in use or has been destroyed by incineration⁽¹²⁹⁾. The major releases are estimated to be 3×10^7 Kg to the air, 6×10^7 Kg to fresh and coastal waters and 27×10^7 Kg to dumps and landfills. The chlorinated biphenyls are believed to be concentrated in several major areas: (1) buried in landfills and dumps; (2) attached to sediments in rivers and lakes, (3) attached to sediments on the continental shelf and (4) distributed over land and sea by aerial fallout and disposal from ships.

3.10.2 Reactivity Studies -

One possible route of degradation for PCBs is through photochemical reactions. Pesticides have been shown to undergo photochemical transformation to sometimes even more toxic substances than their precursors^(130,131). Two halocarbon pesticides, aldrin and dieldrin, have been shown to undergo photo-isomerization via both sunlight and laboratory irradiations⁽¹³²⁾. The products were 2-3 times more toxic than the original compounds.

Examination of the ultraviolet absorption spectra of a few chlorinated biphenyl isomers shows that the onset of absorption occurs around 310 nanometers⁽¹³³⁻¹³⁷⁾. (See Figures 3 and 4). The absorption of the biphenyl structure beginning in the longer wavelengths and continuing to its first major absorption peak between 240 nanometers to 260 nanometers (depending on the chlorine substitution) is generally attributed to

FIGURE 3

ULTRAVIOLET ABSORPTION SPECTRA OF SOME CHLORINATED BIPHENYLS.

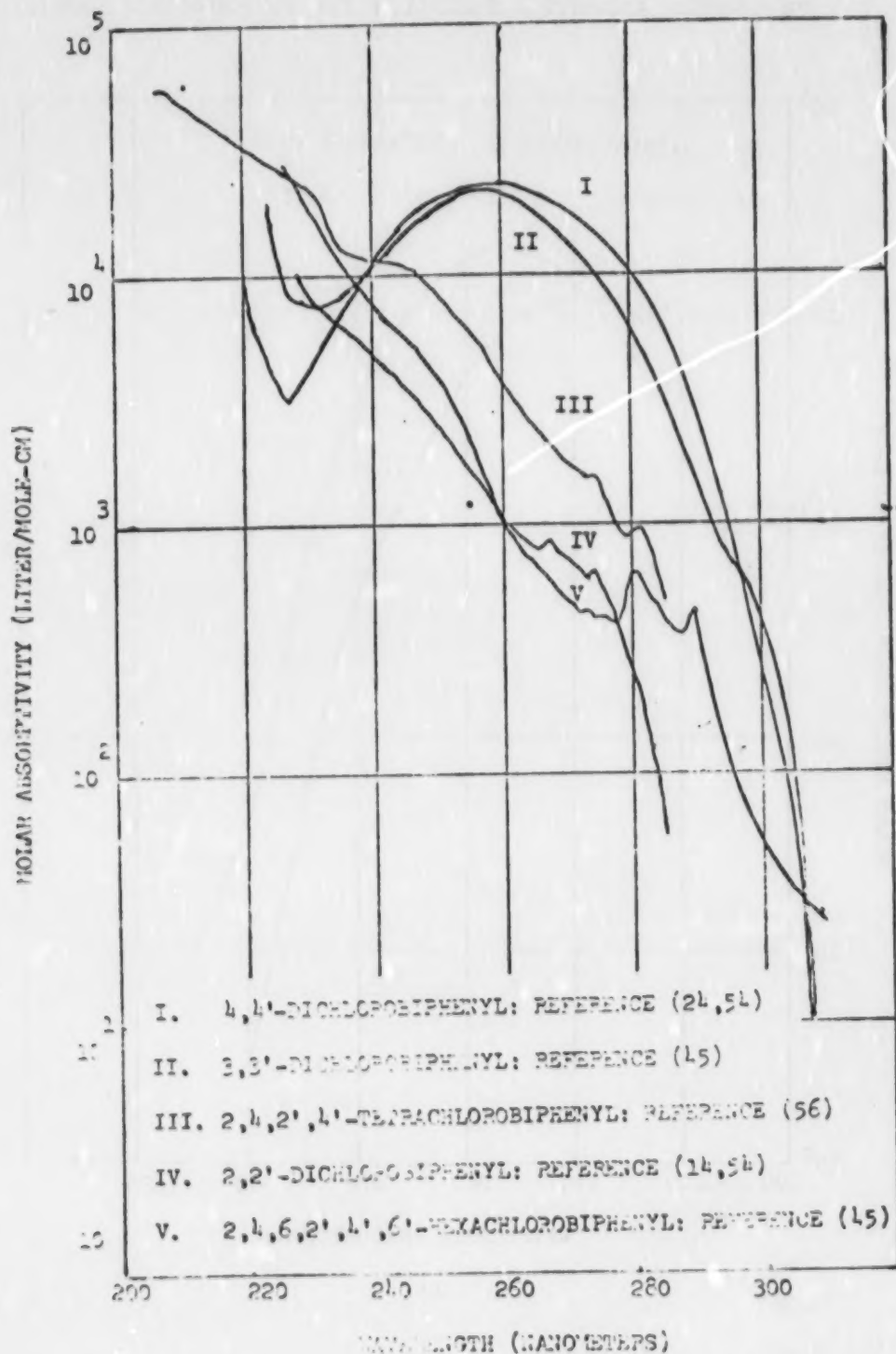
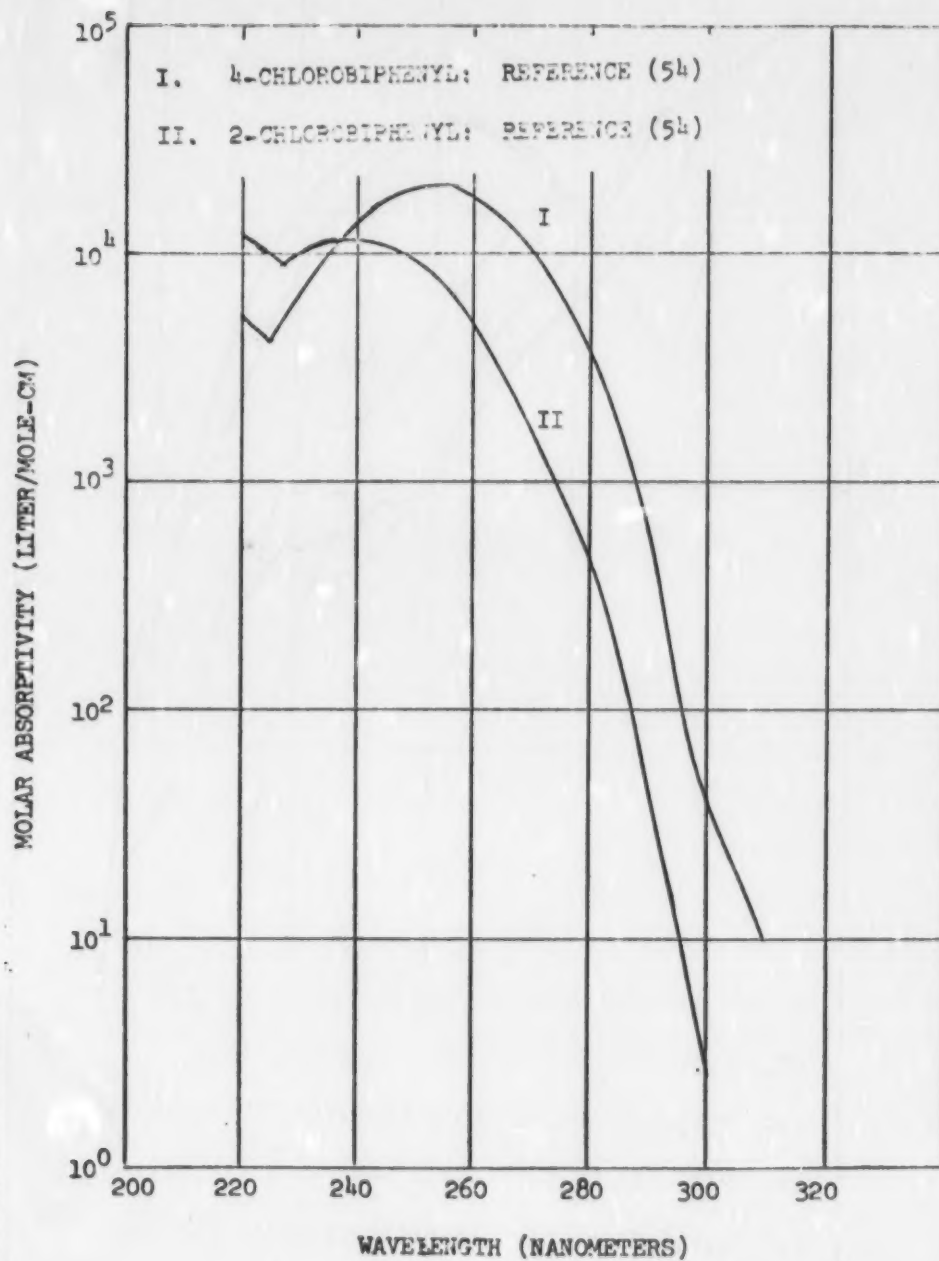


FIGURE 4

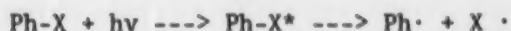
ULTRAVIOLET ABSORPTION SPECTRA OF TWO MONOCHLOROBIPHENYLS.



excitation of the π electrons of the phenyl ring⁽¹³⁸⁾. The appearance of this $\pi \pi^*$ transition peak is clearly defined in the non-ortho substituted isomers but becomes less distinct with increasing ortho-substitution. The isomers of a given series also shows that the ortho substituted isomer exhibits a molar absorptivity of an order of magnitude less than its corresponding meta and para compounds. Figure 4 shows little difference between 3,3-dichlorobiphenyl and 4,4'-dichlorobiphenyl (Note: absorption peak at 257 nanometers) while the 2,2'-dichlorobiphenyl lies at most a full order of magnitude lower. This effect is believed due to the inability of the biphenyl structure to achieve planarity between the rings in the ortho substituted compounds. The relationship of this phenomenon to the excited states and to the reactivity will be discussed later.

Most photochemical studies of PCBs have been conducted in the liquid phase. Usually irradiations have been carried in solvents such as benzene, or light aliphatic alcohols. Concentrations were relatively high (100-1000 ppm). The quantity and purity of UV radiation was generally unspecified except to note that wavelengths were greater than 250 nanometers.

Compounds irradiated include the para substituted chloro, bromo and iodo biphenyls in benzene, chlorobenzene in ethanol and in isopropanol, and O-halonaphthalenes in benzene⁽¹³⁹⁻¹⁴⁵⁾. The results of these studies support a general mechanism for the photolysis of aromatic halides. The absorption of a photon produces an excited species which either returns unreacted to its ground state or homolytically cleaves the carbon-halide bond. This results in the production of a phenyl radical and a halogen atom.



Ph = phenyl, biphenyl or phenyl
naphthalene

X = I, Br, Cl, F (para substitution)

The direct reaction of the Ph-X^* species with another reactant is not believed to occur. The products observed are due to the resulting reaction of the aromatic radical and the halogen atom; hence the products observed are dependent on the nature of the solvent and its impurities. Reactions of the aromatic radical observed include polymerization, hydrogen abstraction, and radical scavenging by oxygen.

The products observed upon irradiation of 4-iodobiphenyl in benzene serve to illustrate the pathways open to the photodissociation products. The identified products include: biphenyl, p-terphenyl, iodine, and 4-hydrozybiphenyl^(141,142). The distribution of these products was dependent on the degree to which oxygen was initially present in the solvent. Upon removal of oxygen, the hydrozybiphenyl decreased along with an increase in the biphenyl/terphenyl ratio⁽¹⁴²⁾. The observed effects are explained by the following mechanisms:

- 1) $\text{C}_6\text{H}_5\text{-C}_6\text{H}_4\text{I} + h\nu \text{ ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_4\cdot + \text{I}\cdot$
- 2) $\text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{C}_6\text{H}_4\cdot \text{ ----> } \text{C}_6\text{H}_5\text{ -- } \text{C}_6\text{H}_4$  (A)
- 3) $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_4\cdot \text{ (A) ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}_6\text{H}_5$
- 4) $(\text{A}) + \frac{1}{2} \text{I}_2 \text{ ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{C}_6\text{H}_5 + \text{HI}$
- 5) $\text{C}_6\text{H}_5\text{C}_6\text{H}_4 + \text{HI} \text{ ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_5\cdot + \text{I}$
- 6) $2 \text{I}\cdot \text{ ----> } \text{I}_2$
- 7) $(\text{A}) + \text{O}_2 \text{ ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_6\text{C}_6\text{H}_5 + \text{HO}_2\cdot$
- 8) $\text{C}_6\text{H}_5\text{C}_6\text{H}_4\cdot + \text{O}_2 \text{ ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{OO}\cdot$
- 9) $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_4\text{OO}\cdot + \text{HI} \text{ --> } \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{OOH} \text{ ----> } \text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{OH}$

Similar results are obtained upon irradiation of chlorobenzene in ethanol or isopropanol⁽¹³⁹⁾. These solvents are excellent hydrogen donating compounds⁽¹⁴⁶⁾. Thus, upon cleavage of the carbon-chlorine bond, the phenyl radical can easily abstract an alpha hydrogen from the alcohol. This results in the quantitative formation of benzene and some hydrogen chloride. Small amounts of ortho, para, and meta chlorobiphenyl were formed also when ethanol was the solvent. No phenols were observed since the solvents were deoxygenated or saturated with high purity nitrogen.

The foregoing limited knowledge of the photochemistry of chlorinated biphenyls coupled with the current concern over PCBs in the environment has prompted a few investigators to conduct studies specifically aimed at elucidating the photochemistry of PCBs in the environment. These studies published since August 1971 through June 1974 are mainly qualitative in nature; they were conducted to determine mechanisms and products. All but the most recent do not attempt to determine product balances or kinetics. The studied PCBs include both individual pure isomers (symmetrically substituted di, tetra, hexa, and octa isomers) and a 54% chlorinated biphenyl commercial mixture. The sample varied in concentration from 1 ppm in solution to some solid film studies. Two investigations involved vapor phase irradiations. The sample conditions for the most part were not typical of environmental conditions; the solvents were chosen mainly for their ability to solubilize the isomer and for their ultraviolet transparency. Some of the studies used sunlight but most used mercury vapor lamps having a maximum ultraviolet energy output at about 310 nanometers which is normally found in the troposphere. However, most of the studies do not define the intensity at these wavelengths, hence, comparison among experimenters or normal tropospheric conditions is impossible. Irradiation times vary from 5 minutes in some laboratory studies to 2 months under natural sunlight.

The conditions and results of the various studies are compiled in Table 3.

Table 3A. Previous PCB Studies - Summary of Conditions and Results

Compound:*		2,4,6,2',4',6'		Hexachlorobiphenyl		Same		Same	
Reference	Solvent	hexane	methanol	methanol	methanol	methanol	hexane, methanol methanol/H ₂ O, acetone	probably	Same
O ₂ Present		probably	probably						
Conc. Ompd.		12,500 ppm	12,500 ppm					10 ppm	
Irrad. source		Hg vap. lamp	Hg vap. lamp					Hg vap. lamp	
Energy Max.		310 nm	310 nm					310 nm	
Irrad. Time		100 min.	100 min.					100 hr.	
Dechlorination products		di, tri, tetra and penta isomers	di, tri, tetra and penta isomer-					biphenyl, mono, di, tri, tetra, and penta isomers; includ. 4-chloro, 4,4-di, and 2,4,6,2,4 isomers	
Isomerisation products	hexa Isomer(s)	hexa Isomers							
Comments		Oxygenated products unidentified						80 cmpds. detected (ngc/ms) including oxygenated products, p-methoxy products, and and chlorinated methoxy substituted dibenzofurans	

* No carboxy or Hydroxy products formed but polymers present when using 100 hr. irradiation time.

Table 3B.

Compound*	2,4,6,2',4',6' hexchlorobiphenyl	Same	2,5,2',5' tetrachlorobiphenyl
Reference		Same	
Solvent	an "inert" Freon	None. As a solid film	None
O ₂ Present	Probably	Yes	Yes
Conc. Cmpd.	10 ppm	Pure Film	10 ppm
Irrad Source	Hg. vap. lamp	Hg. vap. lamp	Hg vap. lamp
Energy Max	310 nm	310 nm	310 nm
Irrad. Time	100 hr.	100 hr.	100 hr.
Dechlorination products	Yes	Yes	No
Isomerisation products	An heptachloro isomer detected	Heptachloro and octachloro isomers formed	No products detected; only starting material
Comments			

*No Carboxy or Hydroxy products present - nor polymers

Table 3C .

Compound*	3,4,3',4' tetrachlorobiphenyl	4,4'-dichloro biphenyl	2,5,2',5' tetrachlorobiphenyl
Reference			
Solvent	Hexane	Hexane	Hexane
O ₂ Present	Not specified	Not specified	No
Conc. compd	15,000 ppm	15,000 ppm	166 ppm
Irrad Source	Hg vap. lamp	Hg vap. lamp	Hg vap. lamp
Energy Max	310	310	310
Irrad. Time	36 hrs	150 hrs.	89 hrs.
Dechlorination products	4,4'-dichloro and 3,4,4'-biphenyl	4-chloro-biphenyl	dichloro biphenyl

* No Carboxy, Hydroxy or Isomerisation products - nor Polymers.

In spite of the qualitative nature of these investigations, some generalizations can be drawn concerning the mechanisms operative in the photochemistry of PCBs. Irradiations of individual isomers generally yielded mechanistically interpretable products while irradiations of the complex commercial mixtures could only be roughly characterized.

Although as previously noted, rates and percent disappearance of the isomers are not comparable between experimenters due to lack of quantification of light fluxes; experiments conducted with a common light source are useful. When this was the case, rates of disappearance of PCB mixtures were found to differ according to the solvent used⁽¹⁴⁷⁾. Irradiation of 2 ppm of 54% chlorinated biphenyl mixtures were found to disappear at decreasing rates in the order: hexane, water, and benzene⁽¹⁴⁷⁾. This order is believed to be related to the ability of the biphenyl radical to abstract a hydrogen from the solvent. This order is an anomaly since water has the highest H bond energy of any of the three. The insolubility of PCBs in water may contribute to an apparent removal.

The number of chlorines and the position of the chlorines on the biphenyl structure are expected to have an effect on the rate of disappearance. It is expected that due to steric effect, the ortho substituted compounds should eliminate the ortho chlorine faster than the corresponding non-ortho compound. However, upon irradiation at 310 nanometers for 24 hours, the following isomers in hexane (1000 ppm) were still present at the indicated percentages: 3, 4, 3', 4'-tetrachlorobiphenyl - 32%, 2, 6, 2', 6'-tetrachlorobiphenyl - 29%, 2, 5, 2', 5'-tetrachlorobiphenyl - 33%, 2, 4, 5, 2', 4', 5'-hexachlorobiphenyl - 3.8%, and 2, 3, 4, 5, 2', 3', 4', 5'-octachlorobiphenyl - 1%⁽¹⁴⁸⁾. Thus, the only distinguishable effects are that the higher chlorinated compounds tend to degrade more efficiently. The effect of the position on the ring is not apparent.

The most frequently observed result of irradiation of PCB mixtures or individual isomers is stepwise dechlorination. The removal of chlorines is seen in different solvents with both sunlight and 310 nanometer mercury vapor light. Dechlorination, for example, occurred upon irradiation of 2, 4, 6, 2', 4', 6'-hexachlorobiphenyl in hexane where penta, tetra, tri, di and monochlorobiphenyls in addition to biphenyl were formed⁽³²⁾.

Dechlorination is observed along with isomerization and chlorination in situations where one or less hydrogens are available for abstraction from the solvent and no other species are present to react with the dissociated components of the biphenyl. This situation occurs when PCBs are irradiated as pure solids or in degassed solvents such as a chlorofluorocarbon. In this environment the phenyl radical and the chlorine atom have no choice but to recombine or react with other PCB molecules. Thus dechlorination and chlorination occur leading to isomerization.

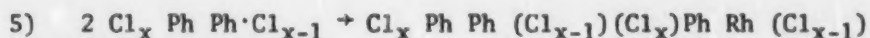
Under prolonged irradiation (90-100 hours) polymers are formed even at concentrations as low as 10 ppm⁽¹⁴⁷⁾. Since chlorination and dechlorination products can again participate in the same dissociation processes

the biphenyl radical can be regenerated.

- 1) $\text{Cl}_x \text{Ph Ph Cl}_x + h\nu \rightarrow \text{Cl}_x \text{Ph Ph Cl}_{x-1} + \text{Cl}^\cdot$ (dissociation)
- 2) $\text{Cl}_x \text{Ph Ph Cl}_{x-1} + \text{Cl}^\cdot \rightarrow \text{Cl}_x \text{Ph Ph Cl}_x$ (recombination)
- 3) $\text{Cl}_x \text{Ph Ph Cl}_x + \text{Cl}(\text{H})\text{Cl}_x \text{Ph Ph Cl}_{x+1}$ (chlorination)
- 4) $\text{Cl}_x \text{Ph Ph Cl}_{x-1} + \text{A} \rightarrow \text{Cl}_x \text{Ph Ph Cl}_{x-1}\text{A}$ (Radical Reaction)

A = Reactant e.g. H, O₂, NO, etc.

Thus the products of these reactions may still be able to further undergo photochemical reactions. But polymerization reactions may also be competing.



In most of the irradiations where oxygen was not removed from the solvent oxygenated products were observed. These were roughly characterized by thin layer chromatographic techniques as being hydroxy and carboxy compounds. When one group of investigators irradiated in methanol they detected 80 compounds via gc/ms⁽¹⁴⁹⁾. Most of the products were oxygenated chloroaromatics - among them a series of methoxy substituted chlorodibenzofurans with 1-5 chlorines and a series of p-methoxy PCBs.

Recent studies have centered upon the nature of the excited electronic states, the mechanisms and the rates of different PCB isomers of the same chlorine content. Nordblum and Miller irradiated 4,4'-dichlorobiphenyl at 310 nanometers in a variety of organic solvents⁽¹⁵⁰⁾. When the 4,4'-dichlorobiphenyl was irradiated in both degassed methanol and 2-propanol, 4-chlorobiphenyl and hydrogen chloride were formed in quantitative yield. The new hydrogen on the 4-chlorobiphenyl was abstracted from the methyl of the methanol as determined by using deuterated methanol. This implies a typical free radical reaction where the weaker C-H bond is broken in preference to the OH bond. Consistent with similar studies it was found that the rate of reactant disappearance was slowed by the presence of oxygen and the product mixture was complex.

The second of the recent studies by Ruzo, Zabik, and Schuetz is a systematic study of the rates and mechanisms of the photoreduction of 6 tetrachlorobiphenyl isomers^(151,152). Again, irradiations at 310 nanometers in both hexane and methanol produced hydrogen chloride, dechlorination products accounting for 90 - 95% of the reacted starting material and between 1 and 3% methoxy substituted biphenyls in the case of the methanolic solutions. The PCBs studied are summarized below.

PCB	Designation
3,4,3',4' - tetrachlorobiphenyl	I
2,4,2',4' - tetrachlorobiphenyl	II
3,4,3',4' - tetrachlorobiphenyl	III

2,3,2',3' - tetrachlorobiphenyl	IV
2,5,2',5' - tetrachlorobiphenyl	V
2,6,2',6' - tetrachlorobiphenyl	VI

The products formed after 20 hours irradiation in hexane and methanol are tabulated below:

PCB	Dechlorinated Product	Methoxylated Products
I	3,4,4' - trichlorobiphenyl 4,4' - dichlorobiphenyl	trichloromethoxy biphenyl
II	2,4,4' - trichlorobiphenyl 4,4' - dichlorobiphenyl 4 - chlorobiphenyl	trichloromethoxybiphenyl dichloromethoxybiphenyl
III	3,5,3' - trichlorobiphenyl	
IV	2,3,3' - trichlorobiphenyl 2,3,2' - trichlorobiphenyl 3,3' - dichlorobiphenyl	trichloromethoxybiphenyl dichlorodimethoxybiphenyl
V	2,5,3' - trichlorobiphenyl 3,3' - dichlorobiphenyl 3 - chlorobiphenyl	trichloromethoxybiphenyl dichlorodimethoxybiphenyl
VI	2,6,2' - trichlorobiphenyl 2,2' - dichlorobiphenyl	trichloromethoxybiphenyl

Examination of the products formed, clearly indicates that ortho chlorines yield products resulting from the loss of these. In their absence, meta chlorines were eliminated and para were the last to cleave. The methanol formed products by attacking at the leaving chlorine position.

Quantum yields of reactant disappearance were also determined for these compounds. These also showed a strong correlation with the position of the chlorines. Compounds I and III, which are non-ortho-substituted, exhibited the least efficiency for reaction. This is believed to relate to the preferred planar geometry for the excited triplet⁽¹³⁸⁾; thus the sterically hindering ortho chlorine leaves preferentially to relieve the strain.

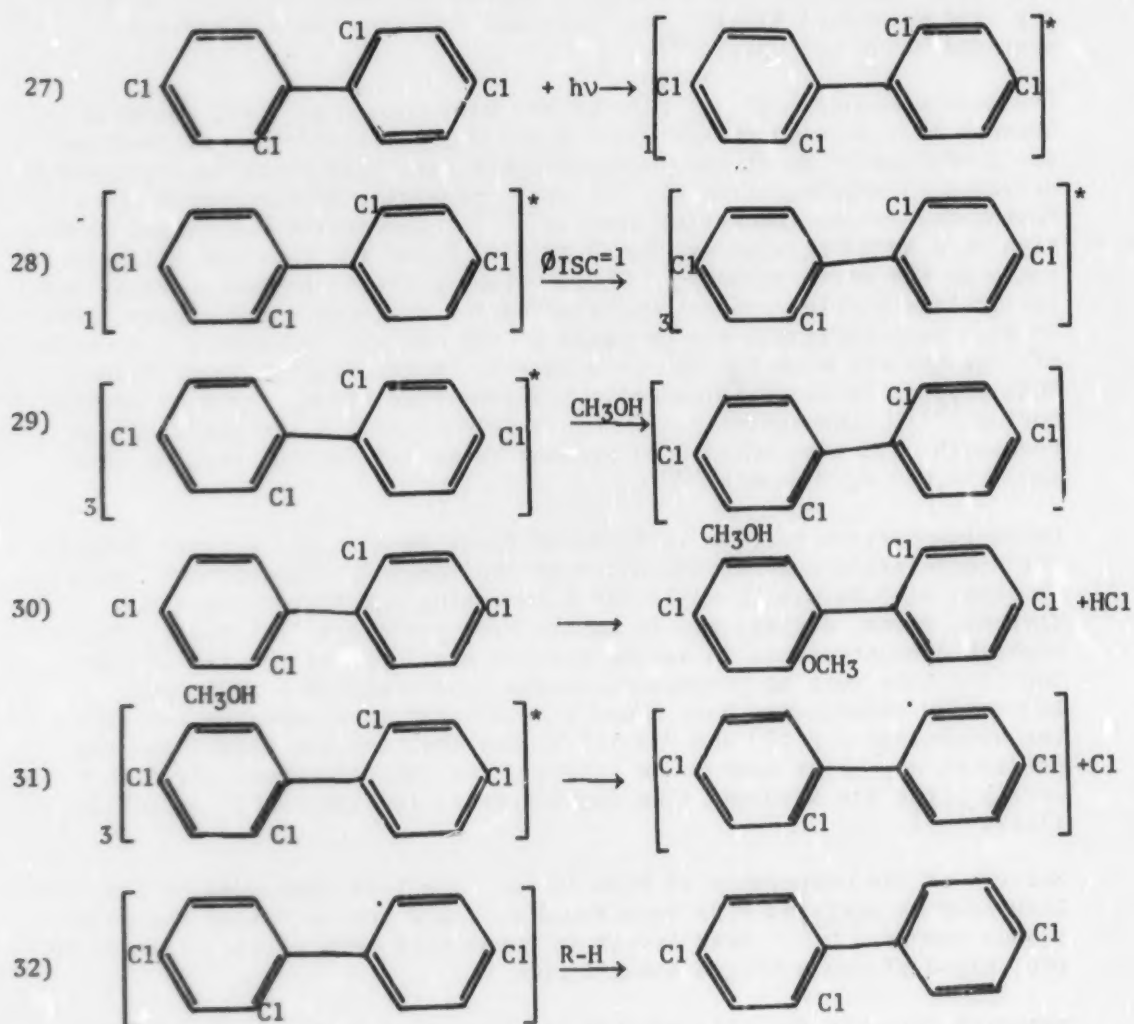
Ruzo et al. also found the triplet to be the excited state⁽¹⁵²⁾. In cyclohexane, the efficiency of intramolecular energy transfer was 100% ($\phi_{isc} = 1.0 \quad 0.05$) for compounds I, II and III. The initial absorption leads to an excited singlet which then quickly leads to the first triplet.

- 1) $[A] + h\nu \rightarrow [A]^*$
- 2) ${}_1[A]^* \rightarrow {}_3[A]^*$

Since the quantum yields are the same for both ortho and non-ortho substituted compounds the process is apparently not affected by planarity of the biphenyl.

The intersystem crossing yield of 1.0 indicates that there are no competing processes for the singlet, i.e., fluorescence, internal conversion. The resulting triplet state is believed to be the reactive species leading to either deactivation, dissociation, or direct reaction. The lifetimes of the triplets also show a correlation with the position of the substituent chlorines. The non-ortho substituted compounds here demonstrate a lifetime 3 times longer than the corresponding ortho substituted compounds; but they also demonstrate a rate about 10 times slower to react than the ortho substituted compounds and a deactivation rate constant 3 times slower than the ortho compounds.

Ruzo et al. proposed the following scheme for the reactions they observed.



Presumably the reaction of the biphenyl radical with oxygen would also account for the observed phenolic compounds found by other investigators; it should be noted, however, that if collision of the excited species (the triplet) with oxygen occurs before dissociation of the oxygen an excellent triplet quencher will lead to the deactivation of the triplet to the ground state.

3.10.3 Ambient Measurements -

A recent review of published measurements of PCBs in surface waters found PCBs quite ubiquitous. A background level for unpolluted fresh waters averaged about 0.5 ppt.⁽¹²¹⁾; the Great Lakes averaged about 5 ppt. Moderately polluted rivers and bays yielded a common value of 50 ppt., e.g. the Milwaukee River. Very polluted Japanese and U.S. rivers averaged about 500 ppt.⁽¹⁵³⁾.

Few direct measurements of PCBs in air have been made. EPA measured between 1 to 50 nanograms/M³ in 4 major U.S. cities⁽¹²¹⁾. Another survey conducted by Woods Hole Oceanographic Institute found an exponential decrease in concentration of PCBs with increasing distance from the Boston-New Jersey industrial complex⁽¹⁵⁴⁾. Concentrations ranged from a high of 5 Ng/M³ at Vineyard Sound to 0.05 Ng/M³ two thousand kilometers out over the north Atlantic. These values reflect the sum of vapor and particulate samples and are uncorrected for collection efficiency. Other studies have indicated the presence of PCBs in air indirectly. A study of organochlorine pesticides in rainwater in the British Isles found PCBs present in all samples collected from 7 stations over a 12 month period⁽¹⁵⁵⁾. Concentrations were not determined. A similar study in the south of Sweden noted PCBs present in aerial fallout ranging from 600 - 10,000 Ng/M³/month⁽¹⁵⁶⁾.

Extensive surveys of PCBs in fish and birds demonstrate a clear tendency for accumulation and magnification in food chains. The highest concentrations of PCBs are found in the fish eating and scavenging birds (herons, terns, eagles) and in marine bird predators (falcons). The highest concentrations in marine systems are found in the fat of the top predators such as porpoises, sharks, and seals (6 - 1800 ppm). Laboratory experiments have shown that aquatic invertebrates and fish can accumulate 3×10^3 and 7×10^4 higher than ambient water; the top predators may be as much as 10^7 higher than ambient water. If fish-eating birds are involved then magnification as high as 10^8 or 10^9 is likely⁽¹²¹⁾.

Surveys of the occurrence of PCBs in man have been conducted by EPA. Of 2189 samples analyzed PCBs were found at 1 - 2 ppm in 30% of the adipose tissue samples⁽¹⁵⁷⁾. Mean levels in human milk were of the order of 60 ppb; blood plasma averaged about 2 ppb.

Research into the toxicity of PCBs has been complicated by the variation in composition from manufacturer to manufacturer and even from batch to

batch; in addition some commercial mixtures are known to contain toxic contaminants such as p-chlorodioxins and chlorinated dibenzofurans⁽¹²¹⁾.

Low level feeding of PCBs to rats demonstrates a tendency for accumulation in the fat⁽¹²¹⁾. Once feeding has ceased as long as 240 days may be required until the concentration in the fat reaches a peak. A half-life of 30 days has been observed in decreasing the concentration. Hydroxylated metabolites have been observed. LD₅₀ for rats were of the order of 5 - 10g/kg. No deaths have ever been directly attributed to PCBs in man.

Chronic intake of small daily doses of 10mg/kg over 50 days causes chloracne in man⁽¹²¹⁾. Reproductive effects have been observed in chickens at 8 ppm continuous feeding and in fish at 0.9 ppb in ambient water.

Release of PCBs to the environment from 1929 until 1970 has been largely unregulated. The American Conference of Governmental Industrial Hygienists recommended a TLV of 1 mg/M³ and 0.5 mg/M³ for biphenyls of 42 and 54% chlorine content respectively⁽¹²¹⁾.

After 40 years of production Monsanto, under pressure from scientists and government, voluntarily initiated a PCBs policy of sale only to customers of closed system use. This largely stopped sales for such applications as paints, papers, plasticizers, sealants, and adhesives, leaving only controlled use in electrical capacitors and transformers. Spent capacitors and discarded transformer oils could be returned to Monsanto for incineration.

On July 16, 1973 EPA and the FDA, in response to a report by CEQ and OST recommending discontinuation of the use of PCBs in all but electrical uses, announced policies concerning PCBs in industrial effluents and tolerable limits in foods and its related packaging⁽¹⁵⁸⁾. EPA placed PCBs on the toxic substances list as defined in the Federal Water Pollution Control Act of 1972; it also announced it would limit discharge of industrial wastes such that PCBs would not exceed 0.01 ppb in rivers and lakes. The FDA simultaneously announced a temporary tolerance level of 2.5 ppm in milk and dairy products, 5 ppm in poultry, and 0.2 ppm in baby foods. Also it banned the use of PCBs in plants manufacturing or storing animal feeds, foods, and food packaging.

PCBs have drawn sufficient concern to activate some international measures.

The World Health Organization in December 1972 announced it was studying the health effects of PCBs and intends to issue environmental health criteria⁽¹⁵⁹⁾. In February 1973 the Organization for Economic Cooperation and Development representing Japan, Australia and the industrial nations of Western Europe and North America adopted a directive calling upon its members to limit the use of PCBs to transformers, capacitors, heat transfer fluids (in other than food, drug, and feed operations),

and hydraulic fluids for mining equipment; they also called for control of the manufacture, import, and export of product containing PCBs⁽¹⁶⁰⁾.

3.11 Review of G.C. Analytical Procedures for Halocarbons

The literature that exists for gas chromatographic halocarbon analysis deals primarily with separations at relatively high concentrations characteristic of quality control production requirements. Reed⁽¹⁶¹⁾ evaluated the resolving power of a number of stationary liquid phases for fluorocarbons and reported the ethyl ester of Kel-F acid 8114 to be the most effective. Dresdner et al.⁽¹⁶²⁾ used the same packing to analyze 6- and 12- carbon fluorocarbon derivatives of SF₆. Ellis et al.⁽¹⁶³⁾ used a packing of Kel-F oil on Fluon powder to separate reactive inorganic compounds such as ClF, HF, Cl₂, ClF₃, UF₆ and Br₂. Mixtures of nitrogen trifluoride with CF₄ were investigated by Nachbaur and Engelbecht⁽¹⁶⁴⁾ using moist silica gel with hydrogen as carrier gas at 0°C. Campbell and Gudzinowicz⁽¹⁶⁵⁾ used diisodecyl phthalate and Kel-F No. 3 oil on Chromosorb W with 1/4 inch columns of varying lengths to measure several fluorocarbons and sulfur fluoride compounds. Clemons and Altshuller⁽¹⁶⁶⁾ determined the relative responses of an EC detector to a number of halocarbons and sulfur halides using a Baymal or an SF 96 column for separation. Greene and Wachi⁽¹⁶⁷⁾ used CH₂=CHCO₂(CF₂-CF₂)₃H coated on Chromosorb W for the separation of several low molecular weight fluorocarbons and Lysyj and Newton⁽¹⁶⁸⁾ found several packing of halogenated polymers plasticized with halogenated oils useful for the separation of some halocarbons. Williams and Umstead⁽¹⁶⁹⁾ used Porapak Q and S in an on-line column concentrating device with temperature programming to separate several halocarbons. Low concentration mixtures (10 to 20 ppb) were concentrated to ppm levels (1 to 2 ppm) and then measured by GC using a microcoulometric detector. This detector was preferred to the electron capture (EC) detector because of the latter's narrow linear range, lack of sensitivity to some compounds, and extreme sensitivity to others.

Priestley et al.⁽¹⁷⁰⁾ developed a GC method for phosgene using an EC detector. An aluminum column packed with didecyl phthalate on GC 22 Super Support provided good separation. Jeltres et al.⁽¹⁷¹⁾ used a similar packing (diisodecyl phthalate) to determine phosgene and dichloroacetylene in air at their subthreshold limit values.

Analytical methods for SF₆ and a limited number of halocarbons have been developed for meteorological tracer studies^(20,172,173,174). Lovelock⁽¹⁷⁵⁾ measured background concentration of ambient CCl₃F, CCl₄ and CH₃I over the North and South Atlantic using a silicone stationary phase and a novel coulometric system. Hester et al.⁽¹⁷⁶⁾ used a stainless steel column containing Na₂SO₄ on Porosil A and temperature programming to measure CCl₃F and CCl₂F₂ in Los Angeles. The presence of atmospheric CCl₄, trichloroethylene and tetrachloroethylene was reported. However, based on the chromatogram presented, better resolution of components would be necessary for accurate analysis.

SECTION IV

EXPERIMENTAL

4.1 Reactors

4.1.1 Teflon bags and Myler bags -

4 ft. x 4 ft., five mil FEP Teflon bags were manufactured in the laboratory. Teflon film in roll form from DuPont was folded over and heat bonded on three edges with a 1/4" wide thermal-impulse heat sealer from Vertrod, Inc. of Brooklyn, N.Y. Some compounds (C114, 111T, F-11, F-12, F113) were found to permeate through Teflon. In these cases identical bags of Myler were manufactured and used. These compounds did not permeate through Myler. The volume of the bags when filled was 200 liters (Teflon) or 144 liters (Myler). Both bags were equipped with two ground-glass ports for filling and sampling, and both were transparent to the wavelengths of the incident light. Irradiations were performed by exposing the aluminized Myler-backed Teflon bags to a bank of 24 48" rapid start 40-watt fluorescent lamps. Mounted side by side the lamps formed a wall 52" x 52". The bank was enclosed by 4 walls (extending 22" outward), which along with the reflectors of the lamp fixtures were covered with reflective aluminized Myler. Thus the side opposite the light bank was open in order to accommodate the Teflon bag. Four small electric fans were mounted in the walls in order to ventilate excessive heat generated by the lamps.

The use of 3 different types of fluorescent lamps permitted the approximation of the quality and quantity of middle and near ultraviolet radiation found in the lower troposphere. Twelve G.E. F40 BLB, 6 G.E. F40 BL and 6 Westinghouse FS40 fluorescent sunlamps were evenly distributed across the 24 mounts. The F40 BLB and F40 BL lamps emit most of the UV energy around 360 nanometers. The middle ultraviolet was supplied by the FS40 sunlamps which emit their peak energy around 310 nanometers. K_1 for Teflon bag irradiations was 0.39 min.^{-1} , and for Myler bags was 0.28 min.^{-1} , due to the lower transmission of Myler. Figure 5 shows the comparative spectral distributions for this array and tropospheric radiation.

4.1.2 Pyrex Reactor -

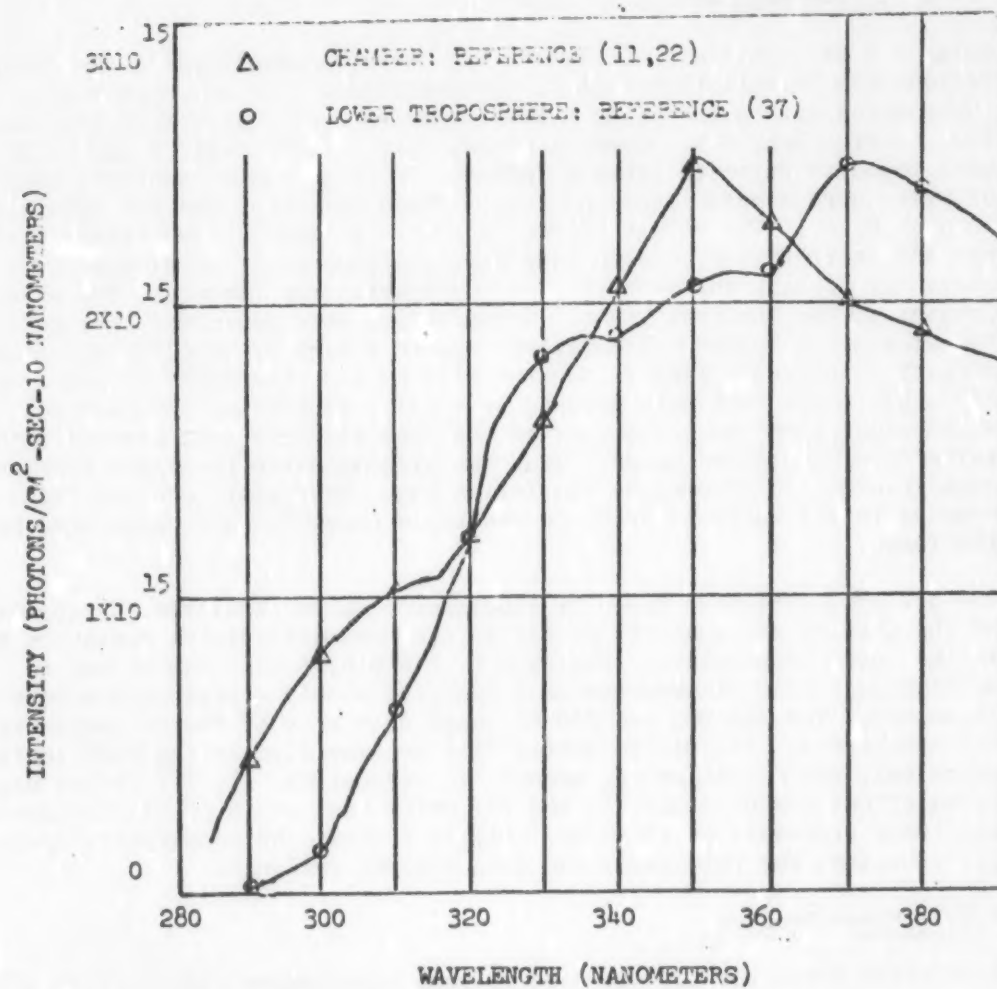
A 72-liter Pyrex reactor was used in some experiments when long irradiation times were desired. It was manufactured by Ace Glass of Vineland, N.J. and was equipped with a thermometer, as well as 3 ports for sampling, filling and venting. An all-glass, magnetic stirrer was enclosed in the sphere to promote mixing. The reactor was used in an air conditioned irradiation chamber equipped with 24 Westinghouse black light bulbs provided by the Environmental Protection Agency. K_1 was 0.3 min.^{-1} .

4.1.3 Quartz Reactor -

A one-liter Hanovia photochemical reactor was used for studies in the U.V.

FIGURE 5

COMPARATIVE SPECTRAL DISTRIBUTIONS: IRRADIATION CHAMBER
VS. TROPOSPHERIC RADIATION.

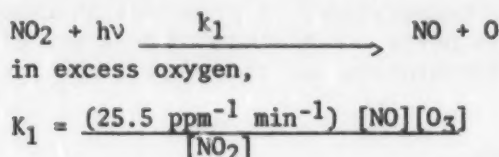


The reactor had a 450 watt high pressure mercury vapor lamp ($>2200\text{\AA}$).

4.1.4 Light Intensity Measurements -

The photolysis of nitrogen dioxide in air was used to measure the light intensity generated by the lamp array used in bag irradiations, and also for the array used with the 72 liter reactor. This measurement was made at 30°C at zero relative humidity and was performed before, after, and in the middle of all the experimental runs.

A 50 pphm concentration of nitrogen dioxide was produced in the bags utilizing the nitrogen dioxide permeation tubes (see Section 4.3). After ten minutes of irradiation, the steady-state concentrations of nitric oxide, nitrogen dioxide and ozone were measured. With K_1 as the reaction rate for the reaction



NO , O_3 and NO_2 concentrations were measured at steady state, and K_1 calculated.

4.2 Preparation of Samples for Irradiation

4.2.1 Materials -

All chemicals were analytical reagent grade, or otherwise the best available.

Ultra-zero air manufactured by Matheson Gas Products of East Rutherford, N.J. was used in all experiments except those in nitrogen. The air was further purified by successive passage through an activated charcoal trap, Ascarite, and molecular sieve. The air so treated had no detectable halocarbon contaminants with the exception of CCl_3F which was present in concentrations of less than 10^{-11}v/v . Analysis showed less than 0.1 ppm total hydrocarbon (expressed as CH_4) and less than 10 ppb NO_x . Pre-purified nitrogen was manufactured by Matheson Gas Products and was further purified by passing it through traps containing activated charcoal, anhydrous calcium sulfate and Ascarite.

The hydrocarbon fuel used in the photochemical experiments was a mixture of paraffin, olefin and aromatic hydrocarbons. It was designated "Fuel A" and was obtained from Exxon Research, Inc.

Its composition was 59.74% paraffin, 13.26% olefin, and 20.98% aromatic hydrocarbons. Detergents and additives, mostly long-chain amino compounds made up the remainder. This fuel mixture was used as a source of free radicals in the simulations. Sufficient hydrocarbon was introduced to the chamber, using a 10 microliter syringe to achieve 1 ppm.

NO₂ was obtained from permeation tubes manufactured by Analytical Industrial Development Co., West Chester, Pa. Allowing one week to obtain thermal equilibrium the tubes were weighed on a Sartorius Analytical Micro-balance and the weight plotted against time. The average leak-rate for nitrogen dioxide tubes was 30,000 nanograms/minute.

4.2.2 Humidity -

50% relative humidity was used in all experiments. It was achieved by injecting the calculated volume of distilled water into the filling gas stream.

4.2.3 Temperature -

A tele-thermometer manufactured by Yellow Springs Instrument Company was used to measure the bag chamber temperature. A probe was inserted into the bag through one of the glass ports. A maximum temperature of 35°C was reached after one hour of irradiation and the temperature remained relatively constant thereafter.

4.2.4 Chamber Filling Procedure -

The Teflon or Myler bags were connected via a ground glass port to the tank of ultra-zero air or N₂ with its train of purifying traps already described. A rotameter (Ace Glass #4-15-2) served to monitor the flow-rate which was generally about 5 liters min.⁻¹. The test substrate, if a liquid, was added to the inner surface of the port, so that the diluent gas passed over it to allow evaporation into the bag.

In other cases, double dilution was used to achieve the desired concentrations, or permeation tubes were used. Double dilution involved injecting a measured quantity of the substrate into a clean four-liter flask through a rubber septum. The flask had two stainless steel balls to facilitate mixing. After allowing five minutes for evaporation and diffusion a 5 cc aliquot was extracted and injected directly into the bag chamber. Permeation tubes are described in Section 4.3.

Nitrogen dioxide was then added by attaching a Teflon line from the permeation apparatus to the bag. The time required for the desired NO₂ concentration to be achieved in the bag (50 pphm) was determined by calculation from the known lead-rate of the permeation tube.

The bag was then mixed by slapping the sides of the bag 30 times. The experiments conducted in bags employed no stirring except this initial mixing of the chamber contents before irradiation. The initial concentrations of ozone, nitrogen oxides, nitric oxide, temperature and the concentration of the substrate were determined (see Section 4.4). The chamber was then placed in front of the light source. Before the irradiation was started, the lamp array was turned on for approximately 30 minutes to allow the lamps to attain constant temperature and thus constant output. Aluminized Myler was attached at the back of the bag

chamber for use as a reflector. Measurements of substrate and product concentrations were then made at 15 minutes, 30 minutes, 60 minutes and at approximately one hour intervals thereafter. In the case of reactive substrates irradiations usually lasted until a decay of one order of magnitude was observed. For very long irradiations the nitrogen dioxide was replenished daily to 50 pphm.

The 72 liter reactor, being a rigid chamber, required special filling techniques. Cleaning was achieved by flushing 10 times the volume of air through the reactor. Double dilution of substrate was employed. After injection, the stirrer was switched on for 5 minutes. Nitrogen dioxide replenishment was achieved by a 200 cc injection of a concentrated nitrogen dioxide mixture derived from a low flow off the permeation tubes into a 1 liter flask. The concentration of 50 pphm was obtained empirically as the small size and rigid nature of the chamber precluded sampling during a run.

Sampling was accomplished by attaching a Teflon line from the appropriate instrument to the bag utilizing ground-glass ball joints for connections and a stopcock to prevent back flow. Gas chromatograph samples were withdrawn through a rubber septum placed in one port by an all glass syringe and immediately injected into the gas chromatograph.

The bags were flushed twice with ultra pure air between each run. Each experiment was duplicated.

4.3 Permeation Tubes

Permeation tubes were calibrated and used to provide known concentrations of several of the compounds studied (F-11, CCl_4 , PCE, TCE, CH_3I , F113 and vinyl chloride) and of NO_2 and phosgene. The permeation tubes were maintained at $30.0 \pm 0.1^\circ\text{C}$ in a water-jacketed mixing chamber except where noted in Table 4. Constant leak rates were usually established within 1 to 2 weeks of conditioning, as indicated by constancy in the rate of weight loss when diluent air at 50 ml. min.^{-1} was passed over them. Table 4 shows the weight loss of the permeation tubes for CH_3I , CCl_4 , CCl_2F_2 , CCl_3F , CH_2ClF , CH_3Cl , $\text{CH}_2\text{ClCH}_2\text{Cl}$, CCl_2 , FCClF_2 , CCl_2CHCl , CH_2CHCl , COCl_2 . Tubes were weighed on an average about 3 times per week using a semi-micro balance.

4.4 Laboratory Analyses

4.4.1 Gas Chromatograph -

The concentrations of the halocarbons were measured by direct injection into a gas chromatograph. Two GC units were used in this study which are referred to as systems A and B. System A was a temperature programmable Fisher-Victoreen 4400 series GC and was equipped with a $15 \text{ mCi } ^{63}\text{Ni}$ EC detector. Full scale deflection (FSD) on a 1 mv recorder was 10^{-13}A . It was operated in the pulse mode (500 usecs). Prepurified nitrogen was used as a carrier gas. A flame ionization detector was used for vinyl

Table 4. Permeation Tube Data

Compound	Tube i.d. (inches)	Wall Thickness (inches)	Temp. °C	Permeation Rate (Ng.cm ⁻¹ min ⁻¹)	% Error (St. Dev.)
CH ₃ I	0.190	0.030	30.0	33.2	1.8
CH ₂ Cl ₂	0.190	0.030	30.0	56.1	3.8
CCl ₄	0.190	0.030	30.0	2.59	15.3
CCl ₂ F ₂ *	0.126	0.125	15.0	463	6.1
CCl ₃ F	0.190	0.030	30.0	110	5.1
CCl ₃ F	0.126	0.062	30.0	53.6	3.7
CH ₂ ClF**	0.126	0.125	30.0	845	9.4
CH ₃ Cl	0.126	0.062	29.3	209	2.2
CH ₂ ClCH ₂ Cl	0.190	0.030	30.0	8.91	4.1
CH ₂ ClCH ₂ Cl	0.126	0.062	30.0	3.95	5.9
CCl ₂ FCClF ₂	0.190	0.030	30.0	60.0	5.3
CClF ₂ CClF ₂	0.190	0.030	30.0	1770	0.9
CCl ₂ CHCl	0.190	0.030	30.0	21.4	4.3
CH ₂ CHCl	0.190	0.030	30.0	386	0.9

* Excessive swelling of tube. Two months before weight loss observed.
 ** 19 days before weight loss linear. 10 days useful lifetime.

chloride with helium as the carrier gas. System B was an isothermal unit equipped with two identical 15 mCi ^{63}Ni EC detectors in series. The electrometer of each detector was connected to one channel of a Soltec dual pen recorder. At maximum sensitivity FSD on a 1 mv scale was $3 \times 10^{-12}\text{A}$. The instrument was operated in a pulse mode (400 μsecs). The operating characteristics of this special purpose instrument have been described in detail⁽¹¹⁾.

Since water vapor would mask important peaks, a 2 in. x 14 in. o.d. Teflon tube filled with Ascarite was routinely inserted (except for phosgene analysis) between the EC detector and all columns used. For Porapak Q above 80°C, the Ascarite was not very effective; however, resolution was adequate. The Ascarite was replaced when the water peak began to appear. All-glass syringes were used since Teflon gas-tight syringes exhibited a continuous bleed of unknown interfering compounds.

4.4.2 Nitrogen Oxides -

Nitrogen oxides ($\text{N} + \text{NO}_2$), nitric oxide and ozone were measured with an Aerochem Model AA - III Chemiluminescence Monitor. The instrument is based on the chemiluminescent reaction of nitric oxide with ozone. The analysis for ozone required a constant source of pure nitric oxide whereas the constant source of ozone for nitric oxide analysis was only dried room air passed through an enclosed ozonator. The analyzer was specific for ozone and nitric oxide; nitrogen dioxide was reduced to nitric oxide in the instrument by passing the sample stream over a heated catalyst and read as total nitrogen oxides. The monitor sampled at 2.4 liters per minute with a 95% response time in 30 seconds.

Calibration was achieved by feeding a known concentration of nitrogen dioxide in air from the permeation tubes and adjusting the potentiometer until the read-out galvanometer was correct. Nitric oxide was automatically calibrated as well due to the 99% efficiency of the catalyst. The Ozone mode was calibrated by performing an internal gas phase titration described in the instrument manual. Double checking was done periodically using both span gases of nitric oxide in nitrogen manufactured by MG Scientific of Kearny, N.J. and the standard Saltzman method⁽¹⁷⁷⁾ for nitrogen dioxide.

4.4.3 Ozone -

Ozone was measured with a Rem Chemiluminescent Ozone Monitor. This monitor is based on the chemiluminescent reaction of ozone with ethylene gas. The reaction produces an excited species whose light signal produced in the photomultiplier is proportional to the ozone concentration. The sampling flow-rate was one liter per minute. The monitor was calibrated by setting the gain control to equal a concentration measured by the neutral buffered potassium iodide standard method. A Rem Ozone Generator was used to generate a steady-state concentration of ozone for calibration and for ozone dark reaction studies.

4.4.4 Light Scattering Aerosol -

This was determined using an MRI integrating nephelometer. Particles of radii between about 0.1 and 10 microns are measured in terms of their scattering coefficient β scat. This is empirically related to the mass loading after subtracting the molecular scattering contribution.

4.4.5 Phenols -

Phenols were collected by absorbing them into sodium bicarbonate solution and analyzing by the colorimetric procedure described by Braverman et al. (178). The analysis was based on the reaction of diazotized p-aminodimethylaniline sulfate with phenolic compounds to form a dye which can be determined colorimetrically. With the collection of a 10:1 gas sample and the use of 40 mm spectrophotometer absorption cells a sensitivity of about 0.1 ppb was realized.

4.4.6 Aldehydes -

Aldehydes were determined by the sulfoxylate method(179). The method is sensitive to aldehydes which will combine with sodium bisulfite to form a non-volatile addition product. The bisulfite is later released and determined to quantitate the aldehydes present.

4.4.7 Phosgene -

Phosgene was analyzed with the Fisher Victoreen gas chromatograph. Separation was achieved using 3 ft. of 1/4" o.d. aluminum packed with 30% didecylphthalate on 100/120 mesh acid washed chromosorb P. A flow of 40 cc/minute nitrogen was maintained through the column along with 90 cc/min of argon/methane (90/10) purge gas through the detector. The oven temperature was operated at 30°C and the detector at 200°C. The detector was operated in the pulse mode at 500 microseconds. The detector was calibrated according to the pulse-flow coulometry method developed by us and described in detail in Section 5.3. With a 10 cc sample the method had a sensitivity of about 0.1 ppb. A calibration curve is shown in Figure 6; standard phosgene concentrations were obtained using a permeation tube.

4.4.8 Chloride and Hydrogen Ion -

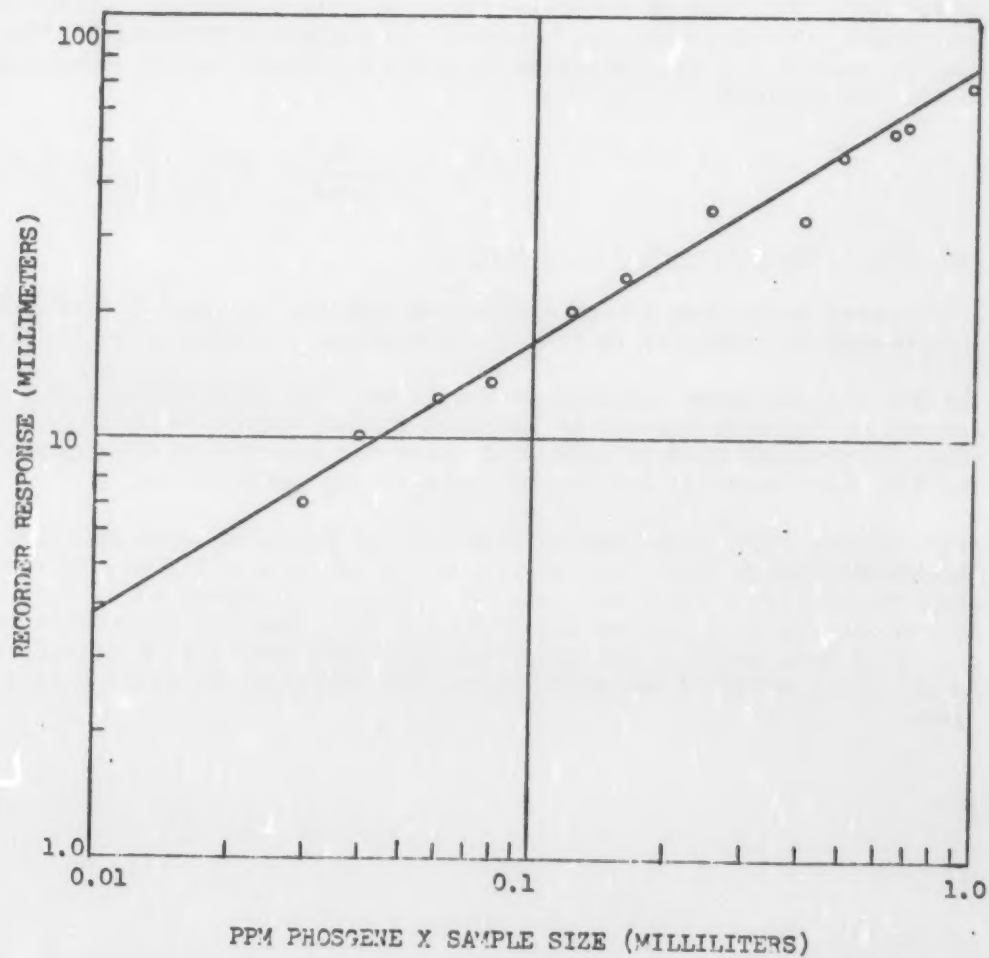
A sampling train consisting of a 5 mm i.d. teflon tube with an 18/7 socket joint, midjet impingers, trap, rotameter, and vacuum pump was used to collect HCl from the bag samples. The gas was drawn through the impingers which were each charged with 5 ml of distilled water, at the rate of 1 liter min.⁻¹ for 10 minutes.

Chloride analysis was performed potentiometrically. A Corning Model 12 Research pH meter equipped with a Coleman 3-802 Ion Selective Electrode and a Corning Double Junction Ceramic Reference Electrode was calibrated

FIGURE 6

GAS CHROMATOGRAPHIC ELECTRON CAPTURE CALIBRATION

CURVE FOR PHOSGENE.



against standard Cl^- solutions at 25°C and were used to measure the Cl^- concentration in impinger samples. The EMF measured was compared against the calibration curve of $\log (\text{Cl}^-)$ vs EMF and the concentration obtained (see Figure 7). The concentration of Cl^- in the sampled gas was calculated by the equation:

$$\text{Concentration } \text{Cl}^- \text{ (V/V, ppm)} = \frac{L \times V_L}{V_g} \cdot \frac{24.4 \text{ liters}}{\text{mole}} \cdot 10^6$$

where L = chloride ion concentration in the liquid analyzed moles/liter
 $V_L = 10^{-2}$ liter = volume of collection water
 $V_g = 10$ liters = volume of air sampled

After the chloride analysis was completed the pH of the same samples were determined. The same pH meter was employed with a Corning Combination pH Electrode. The electrode was standardized against a phosphate buffer. A similar calculation was performed in order to obtain the H^+ concentration in the air sampled:

$$\text{H}^+ \text{ conc in ppm} = \frac{[\text{H}^+] \times V_L}{V_g} \cdot \frac{24.4 \text{ l}}{\text{mole}} \cdot 10^6$$

4.5 Field Analysis - Mobile Laboratory

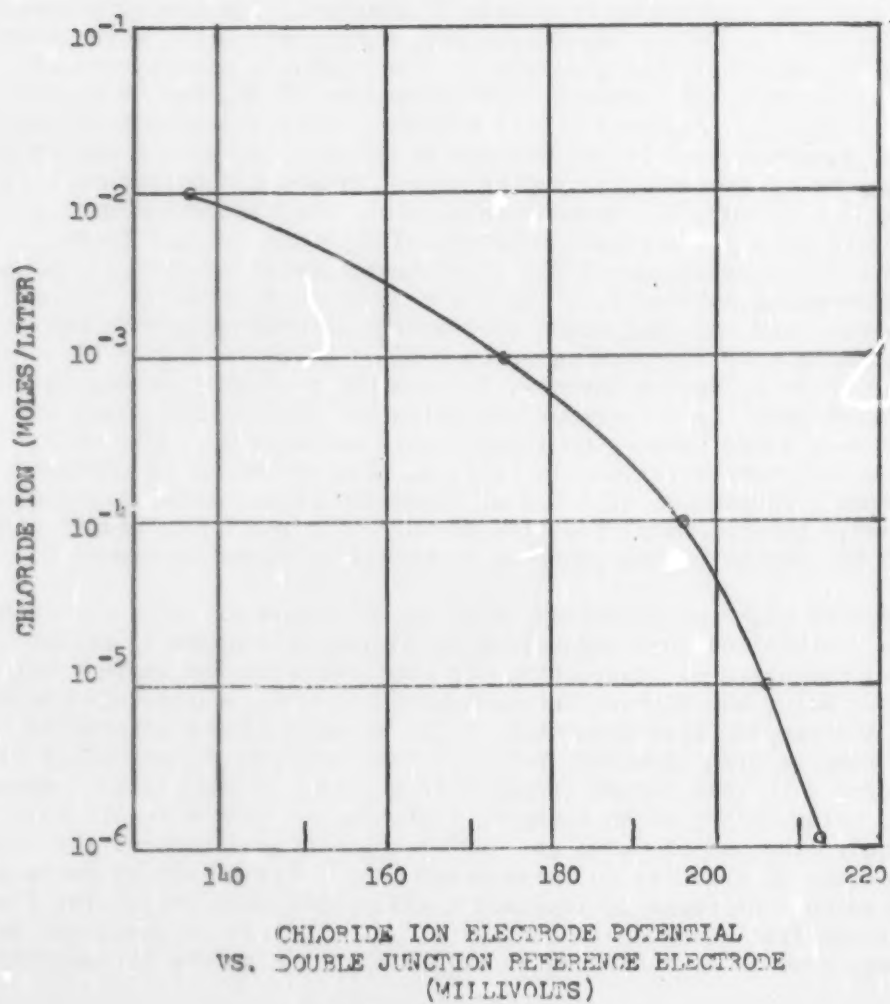
A Winnebago motor home equipped with the required aerometric monitoring instruments was used for on-site field studies initiated after May 1974.

The gas chromatograph equipped with a 10 mCi ^{63}Ni EC detector and a flame ionization detector (system A) was used for halocarbon analysis. The other instruments used in this study were the Aerochem $\text{NO-NO}_x\text{-O}_3$ analyzer, the REM ozone analyzer and the MRI integrating nephelometer.

Prior to May 1974, grab samples from various locations were analyzed in the New Brunswick, N.J. laboratory. One hundred-ml all-glass syringes each fitted with a three-way Luer-Lok valve and a septum were found most convenient for this program and exhibited less than 10% halocarbon loss over a 48 hour period. All-glass syringes were used for GC injections. An all-glass manifold was used for ambient sampling of nitric oxides and ozone.

FIGURE 7

TYPICAL CHLORIDE ION ELECTRODE CALIBRATION CURVE.



SECTION V

GAS CHROMATOGRAPHIC ANALYTICAL PROCEDURES FOR TRACE LEVELS OF

HALOCARBONS AND SF₆

5.1 Column Evaluation

The nine columns used in this study are given in Table 5 and are referred to by their designated numbers. Unless otherwise indicated, data presented here were obtained with System A. The optimal isothermal temperatures for the separation of sub-ppb mixtures with air of SF₆, CBrF₃, CHCl₂F, CCl₂F₂, CCl₃F, CH₃I, CCl₂F-CClF₂, CHCl₃, CH₃-CCl₃, CCl₄, C₂HCl₃, C₂Cl₄, COCl₂ and CH₂=CHCl using the indicated columns, are given in Table 5. For mixtures, optimal temperatures were chosen for adequate resolution combined with minimum total elution time. For single compounds, this elution time was limited to less than 10 minutes. Ppm concentrations of CH₃I, CCl₂F-CClF₂, CHCl₃, CH₃-CCl₃, CCl₄, C₂HCl₃ and C₂Cl₄ were generally required for detection using column 1. The useful chromatograms of ambient injections and synthetic ppb injections of SF₆ and CBrF₃ are given in Figure 8. Figure 8 (C) also demonstrates the effect of purge gas on the EC response to a 19 ppb mixture of CCl₂F₂. Figures 9 and 10 are chromatograms of ambient air samples using Chromosil 310 (column 2) and Carbowax 1500 (column 3), respectively, where the latter includes a chromatogram of a ppb synthetic mixture of CH₂=CHCl using a flame ionization detector (Figure 10B). The chromatograms of typical ambient air samples using columns 5, 6 and 7 are shown in Figures 11, 12 and 13, respectively, and the dual trace coulometric chromatogram obtained with System B using a DC 200 packing (column 8) is given in Figure 14. For a typically polluted day in Bayonne, N.J., ambient concentrations calculated from peak height versus concentration calibration plots are compared with corresponding coulometrically calculated (equation 3, Section 5.2.1) concentrations in Table 6. The chromatogram obtained with column 9 (System B) of a 0.4 ml injection of an irradiated simulated tropospheric photochemical reaction mixture of 1 ppm C₂Cl₄ and 50 pphm NO₂ (50% RH) demonstrating phosgene synthesis is shown in Figure 5.

At relatively high concentrations (10² to 10³ times ambient) the compounds of Table 5 exhibited good separation on Porapak Q (column 1) at the indicated temperatures, suggesting its applicability for ambient halocarbon analysis. Using the Fisher Victoreen GC (System A), chromatographs of ambient air samples (New Brunswick, N.J.) at each of the determined optimum temperatures, however, revealed that only CCl₂F₂ and CCl₃F could be measured with this column (Figures 8A and 8B). Figure 8 also demonstrates, using CCl₂F₂ as an example, a phenomenon common to all halocarbons under study: the use of purge gas (10% methane/argon) reduced the sensitivity of the EC detector to these compounds. This effect of purge gas is attributed to a decrease in ionization efficiency with increasing flow rate as predicted from equation 1, Section 5.2.1. The use of purge gas accordingly would only seem to be indicated at relatively high solute concentrations.

Table 5. Useful Columns and Temperatures for Ambient Halocarbon Analysis

Col. #	Specifications with Comments
1	SS 6' x 1/8"; 80/100 mesh Porapak Q . . . 30°C for SF ₆ and CBrF ₃ , 70°C for CHCl ₂ F, 80°C for CCl ₂ F ₂ , 130°C for CCl ₃ F and CH ₃ I, 135°C for CCl ₂ F-CCl ₃ , 140°C for CHCl ₃ , 165°C for CH ₃ CCl ₃ , 175°C for CCl ₄ , 180°C for C ₂ HCl ₃ and 200°C for C ₂ Cl ₄ .
2	SS 12' x 1/8"; 80/100 mesh Chromasil 310 . . . 23°C for CCl ₂ F ₂ , CCl ₃ F, CCl ₄ .
3	SS 9' x 1/8"; 0.4% Carbowax 1500 on 80/100 mesh Carbowax A . . . 23°C for CCl ₂ F ₂ , CCl ₄ , CH ₂ =CHCl*
4	SS 7' x 1/8"; 20% di-2-ethylhexyl sebacate on 30/60 mesh acid washed (A/W) Chromosorb W . . . 50°C for CCl ₃ F
5	SS 6' x 1/8"; 5% SE 30 on 80/100 mesh Chromosorb W (A/W) . . . 19°C for CCl ₃ F, 23°C for CCl ₂ F-CCl ₃ , CH ₃ CCl ₃ , CCl ₄ , C ₂ Cl ₄ .
6	SS 6' x 1/4"; 10% DC 710 on 80/100 mesh Chromosorb W (A/W) . . . 23°C for CCl ₃ F, CH ₃ I, CHCl ₃ , CH ₃ CCl ₃ , CCl ₄ , C ₂ HCl ₃ .
7	SS 6' x 1/4"; 10% Carbowax 400 on 80/100 mesh Chromosorb W (A/W) . . . 23°C for CCl ₃ F, CH ₃ I, CCl ₄ , C ₂ Cl ₄ .
8.	SS 5' x 1/4"; 10% DC 200 on 30/60 mesh Chromosorb W (A/W) . . . 23°C for CCl ₃ F, CH ₃ I, CCl ₂ F-CCl ₃ , CHCl ₃ , CH ₃ CCl ₃ , CCl ₄ , C ₂ HCl ₃ , C ₂ Cl ₄ , COCl ₂ .
9.	Aluminum 18" x 1/4"; 30% Didecyl phthalate on 100/120 mesh Chromosorb P . . . 23°C for CCl ₃ F and COCl ₂ .

*Flame ionization detector was used for CH₂=CHCl

Figure 8

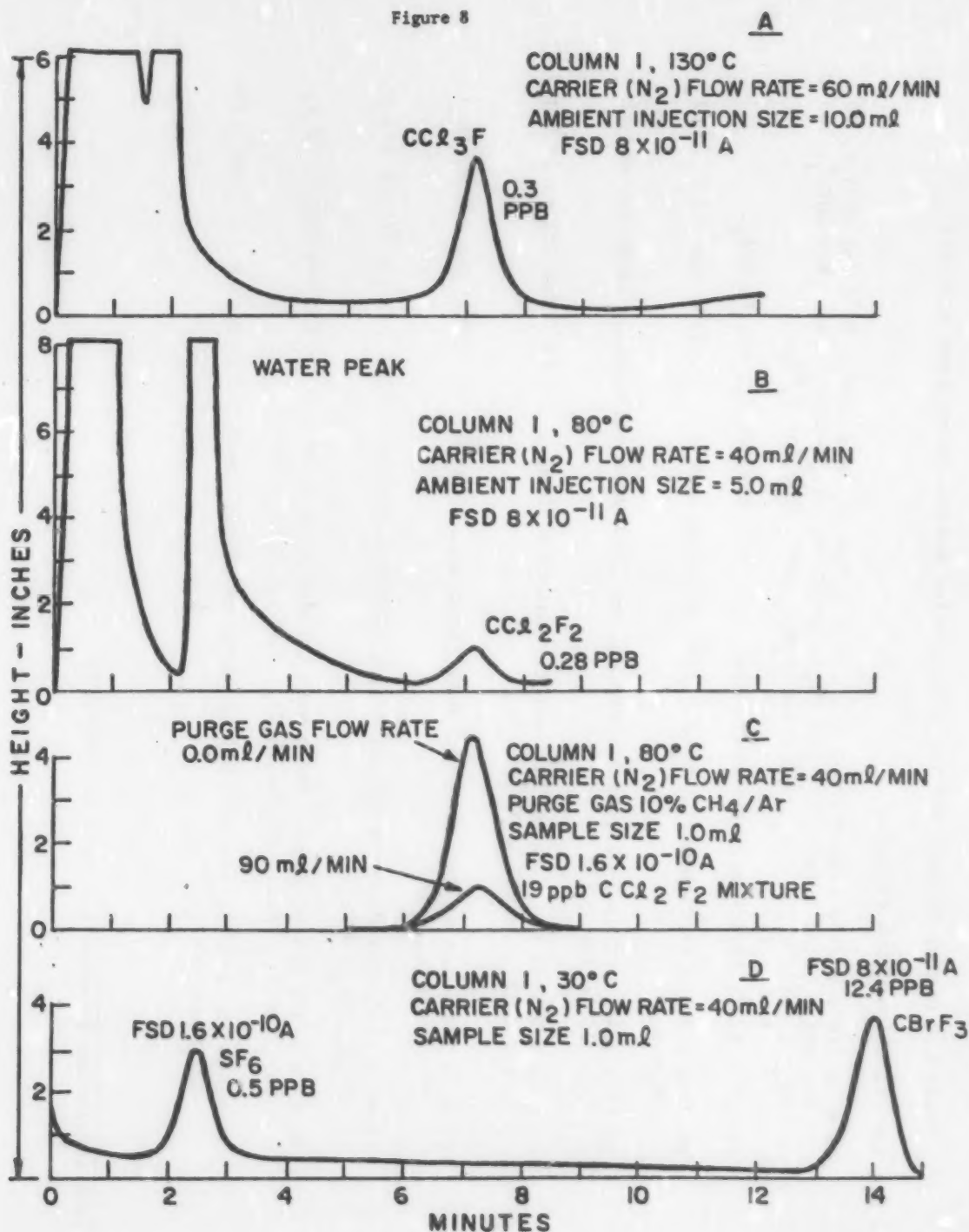


Figure 9

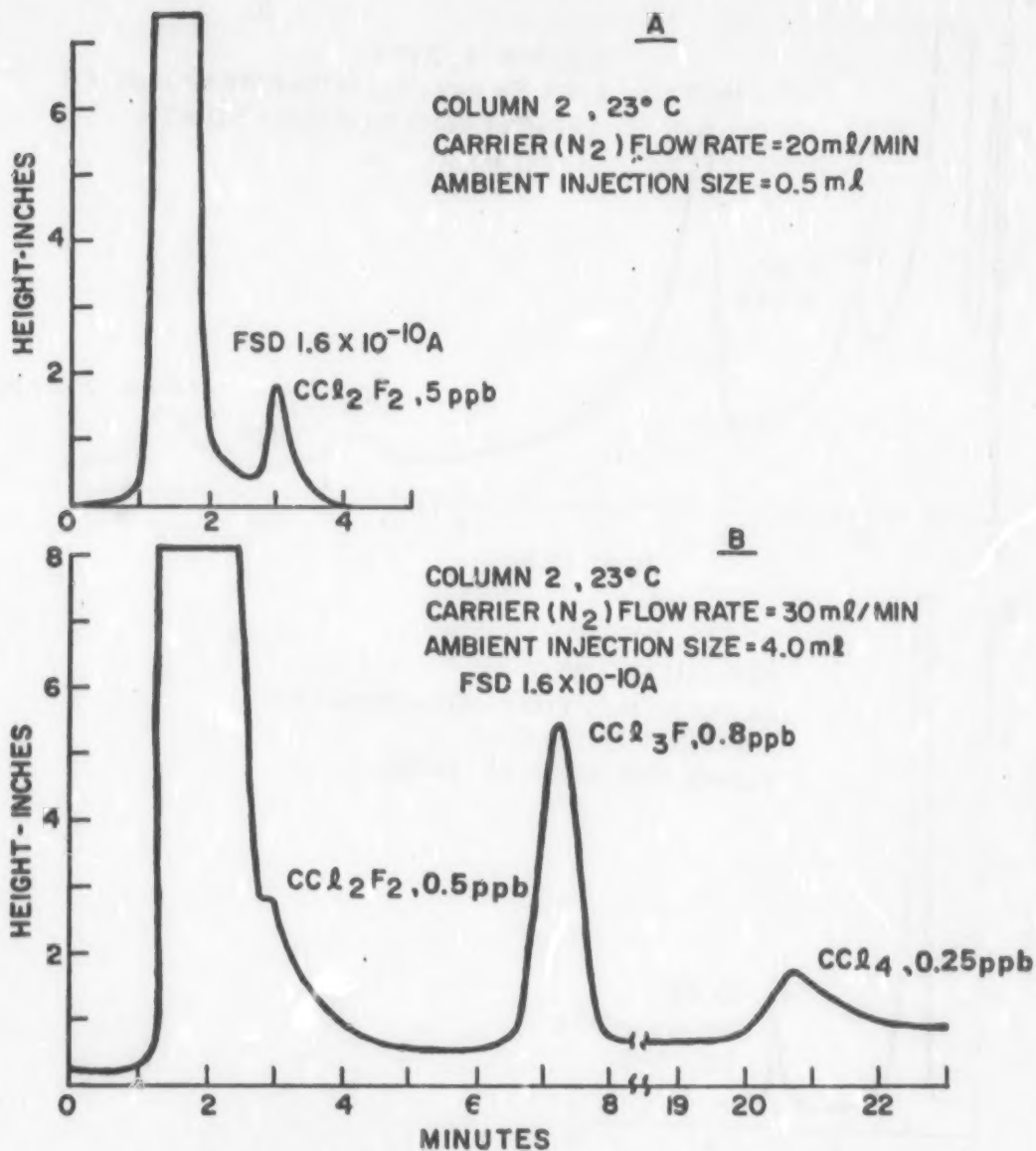


Figure 10

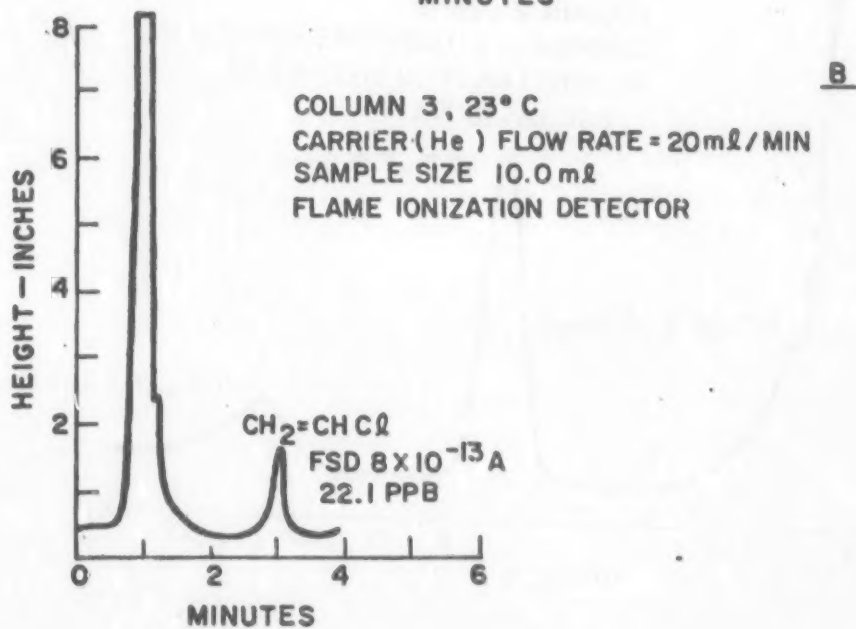
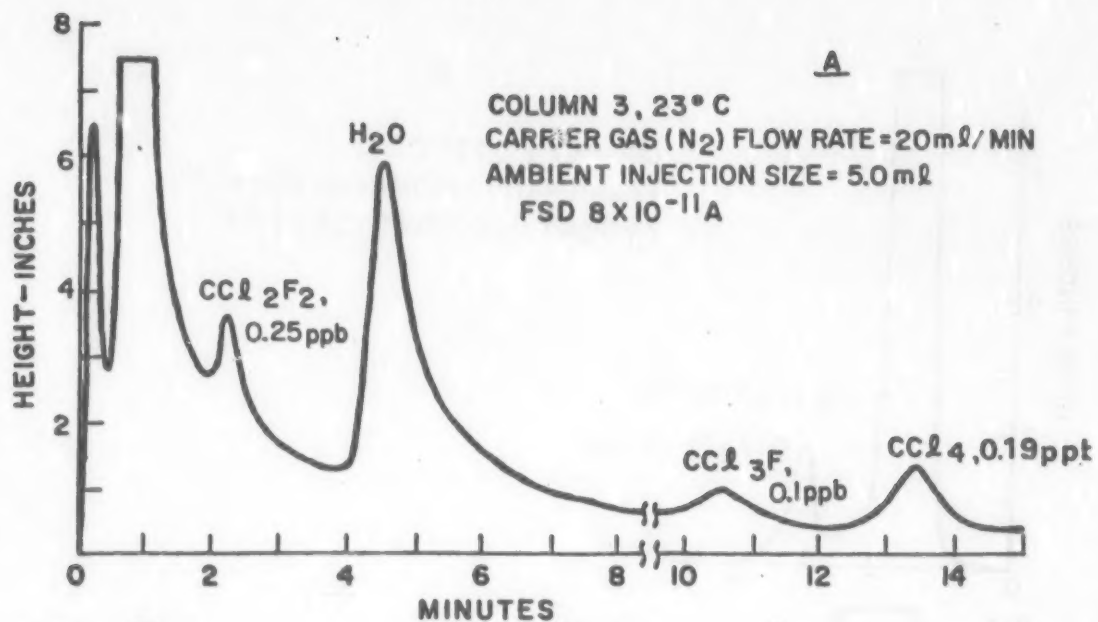


Figure 11

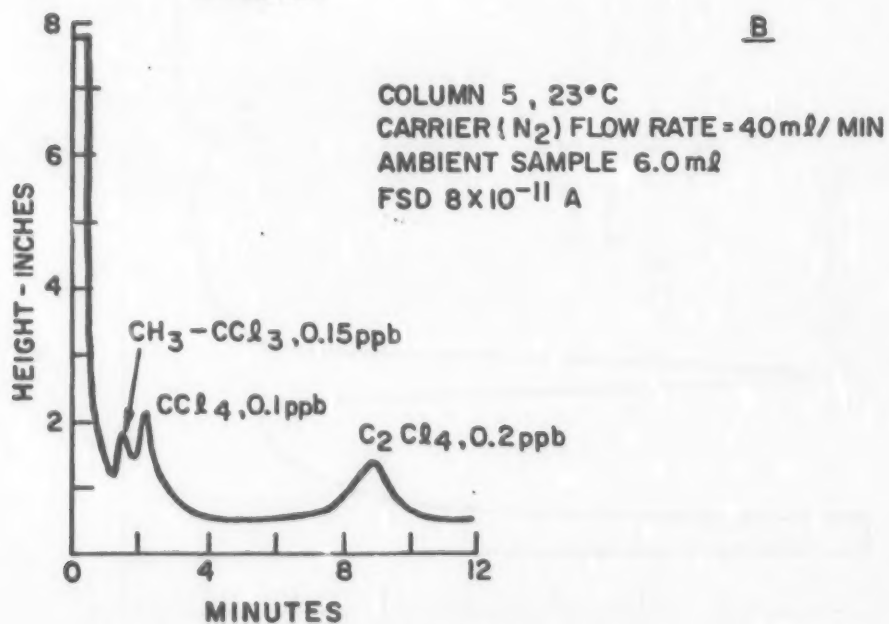
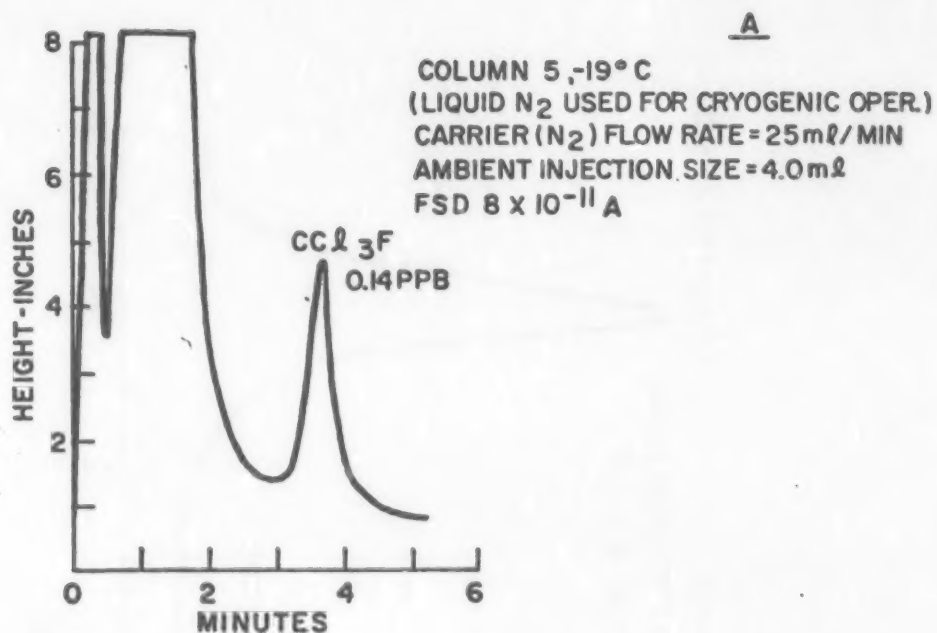


Figure 12

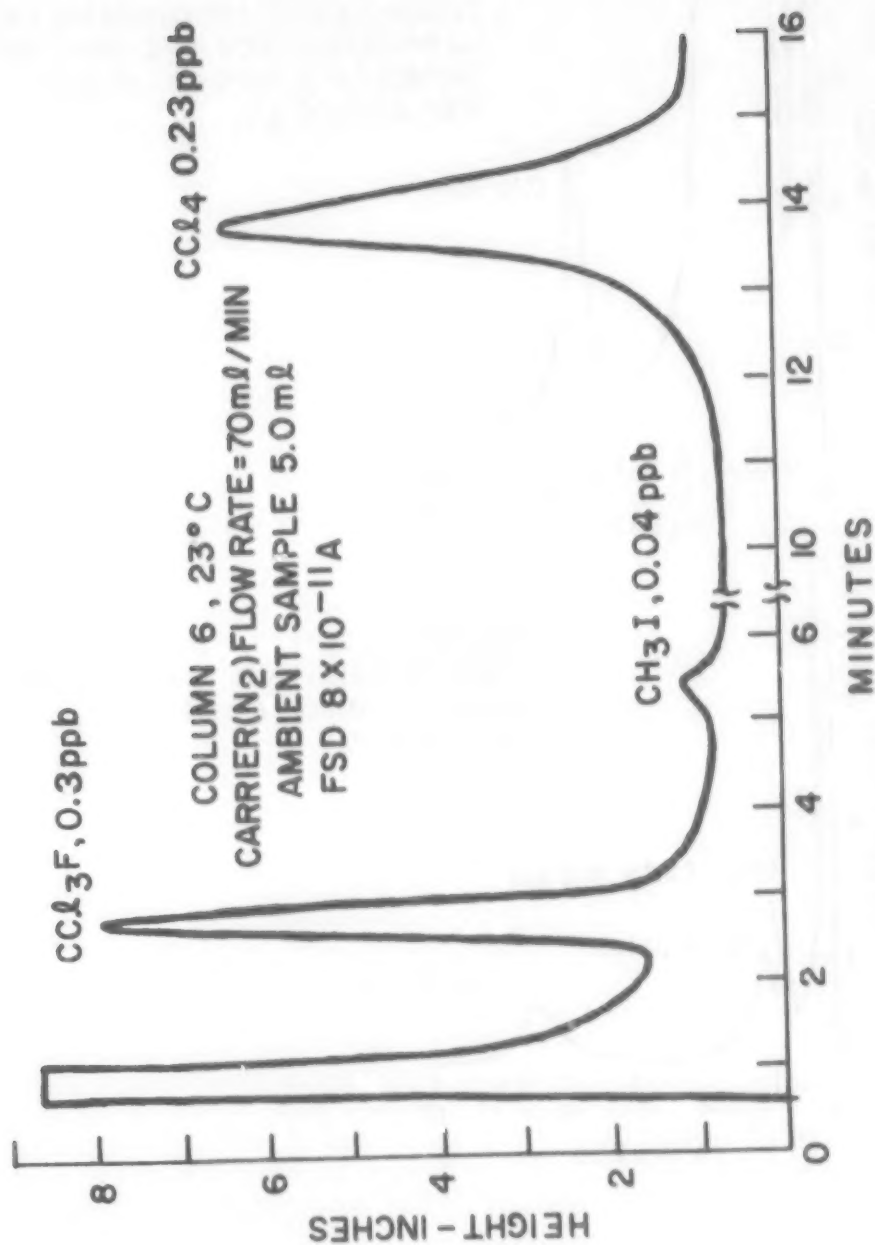
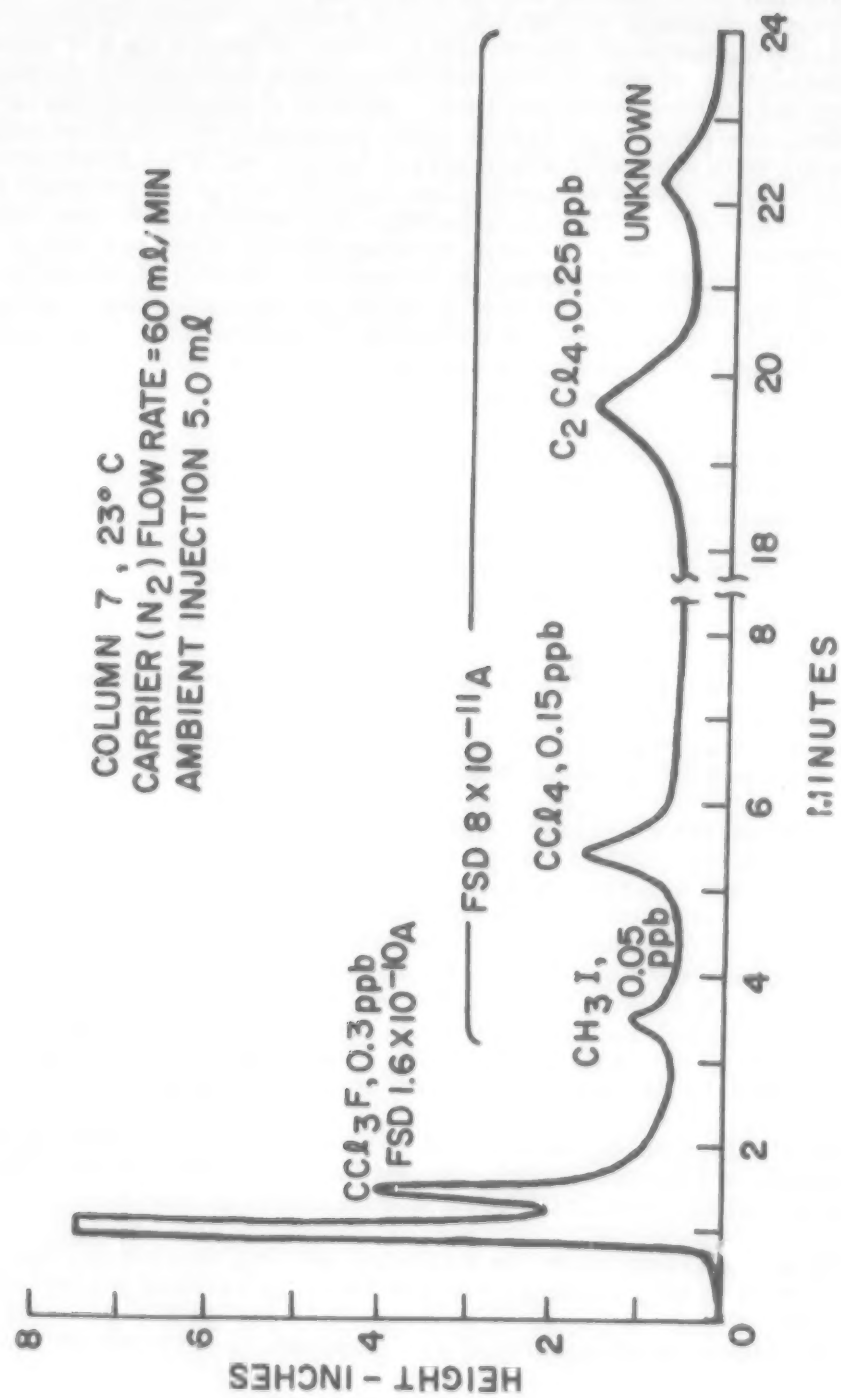


Figure 13



The identity of both CCl_2F_2 and CCl_3F was confirmed early in our experiments by retention data on Chromosil 310 and Carbowax 1500 (Figures 9 and 10). These columns also resolved CCl_4 . Reference to a chromatogram obtained on a similar air sample using DC 200 and System B (Figure 14) clearly illustrates that CH_3I , $\text{CCl}_2\text{F}-\text{CClF}_2$, CHCl_3 , CH_3CCl_3 , CCl_4 , C_2HCl_3 and C_2Cl_4 suffered irreversible losses on the Porapak Q column. Since synthetic mixtures of SF_6 and CBrF_3 could be easily detected above 0.001 ppb and 0.005 ppb respectively, we must conclude that background SF_6 and CBrF_3 are present at levels below these values. This is supported, in part, by Lovelock⁽⁸⁾ who reported background SF_6 concentrations of 1.2×10^{-13} v/v. Based on production figures CHCl_2F is probably present below 10^{-12} v/v also. This is substantially below the EC sensitivity for this compound (15 ppb); however, because of its inertness CHCl_2F should not suffer significant losses on Porapak Q. It should be noted, however, that SF_6 and CBrF_3 , by virtue of their low background concentrations, inertness, excellent electron absorbing properties, and good resolution on Porapak Q at ambient temperatures (Figure 8D), can serve as good tracers for dual source studies.

The recent evidence indicating industrial exposure of workers to vinyl chloride as a possible cause of a rare form of liver cancer known as angiosarcoma supported the inclusion of vinyl chloride measurements in our ambient monitoring program. Since the flame ionization detector was found to exhibit a greater sensitivity to vinyl chloride than did the EC detector, GC conditions were optimized with the former. A sensitivity of 10 ppb was achieved. No detectable vinyl chloride was measured at Sea Girt, N.J.; New Brunswick, N.J.; Sandy Hook, N.J. or New York City (45th Street and Lexington Avenue) during short term monitoring efforts in June 1974. In our current monitoring efforts vinyl chloride concentrations as high as 1500 ppb have been measured in Delaware City, Delaware (intersection of State Road 448 and Route 72).

Based on the excellent separation of air and $\text{CClF}_2-\text{CF}_3$, CH_3-CHF_2 , CCl_2F_2 , $\text{CCl}_2\text{F}-\text{CClF}_2$, CHClF_2 , CCl_3F and CHCl_2F at high concentrations on a di-2-ethylhexyl sebacate packing⁽¹⁸¹⁾ this packing was evaluated for ambient analysis at various temperatures for the compounds under study. Only CCl_3F could be detected, indicating significant sorption of the other compounds by this column. An SE 30 packing on the other hand, was quite useful. With this packing, it was possible to separate, identify and quantify CH_3CCl_3 , CCl_4 and C_2Cl_4 in the ambient air at room temperature (Figure 11). Additionally, CCl_3F could be properly separated from the air peak by cryogenic operation at -19°C (Figure 11).

DC 710 (column 6) facilitated the detection of an unknown ambient compound which subsequently was confirmed as CH_3I (Figure 12). Additionally, this column provided excellent resolution of CCl_3F .

In an ancillary study to determine ambient concentrations of peroxyacetyl nitrate (PAN), Carbowax 400 was found to resolve ambient CCl_3F , CCl_4 and C_2Cl_4 (Figure 13). This finding was fortuitous because it allowed additional confirmation of the compounds identified on the SE 30 column

by virtue of the significantly different characteristics of the two columns. The unknown peak on the chromatogram remains to be identified.

By far the most useful packing for ambient halocarbon analysis was DC 200 (column 8). With this column, excellent resolution was obtained for CCl_3F , CH_3I , $\text{CCl}_2\text{F}-\text{CClF}_2$, CHCl_3 , CH_3-CCl_3 , CCl_4 , C_2HCl_3 and C_2Cl_4 (Figure 14). Additionally, the separations were achieved isothermally at room temperature. Confirmation of compound identity was obtained by use of the previously presented retention data and the novel application of ionization efficiencies. In this, the calculated ionization efficiency (equation 2, Section 5.2.1) of a compound, tentatively identified by retention data, was compared with that of a standard mixture for equality.

The relatively close agreement between the calibrated and coulometrically determined concentrations for CCl_3F , CH_3I and CCl_4 (Table 6), and our experience with coulometric errors as a function of ionization efficiencies, indicate minimal sorption errors for the DC 200 column. For the other compounds, either sorption or coulometric factors⁽¹¹⁾ must account for the discrepancy. As is clear from Table 6, where better agreement is seen with the short column as compared to the long column, a large percentage of C_2Cl_4 error is attributable to column sorption.

Although the tropospheric synthesis of phosgene from halocarbons has been posulated, we are aware of no previous detection of phosgene in simulated smog reactions. As can be seen from Figure 15, phosgene is synthesized during the irradiation of a mixture of NO_2 and C_2Cl_4 with simulated sunlight ($>2950\text{\AA}$ $k_1=0.4/\text{min}$). Confirmation was obtained, using standard phosgene mixtures, with retention data and ionization efficiency characteristics. The discrepancy between the actual (0.28 ppm) and coulometrically determined (0.1 ppm) phosgene concentration is due to sorption or heterogeneous decomposition in the column. Promising research now underway in this laboratory indicates that this sorption problem may be empirically corrected for by inclusion of sorption kinetics in the coulometric analysis.

DC 200 has been demonstrated to be an excellent packing for the separation and EC determination of ambient CCl_3F , CH_3I , $\text{CCl}_2\text{F}-\text{CClF}_2$, CHCl_3 , CH_3-CCl_3 , CCl_4 , C_2HCl_3 and C_2Cl_4 under isothermal (23°C) conditions. Porapak Q at 80°C and Chromosil 310 and Carbowax 1500 at 23°C were found acceptable for ambient CCl_2F_2 analysis. Porapak Q at room temperature is also a very good column for the separation of SF_6 and CBrF_3 . Carbowax 1500 exhibited excellent resolution of vinyl chloride at room temperature (23°C). Phosgene was found to suffer unacceptable irreversible losses in all columns studied except didecyl phthalate. This column provided excellent resolution at 23°C and sorption losses, even though substantial, were sufficiently small to allow accurate analysis in the sub-ppb range with frequent calibration.

On a typically polluted day all halocarbons under study could be measured in the sub-ppb range. As will be reported later, CCl_2F_2 , CCl_3F , CH_3I , CH_3CCl_3 , CCl_4 and C_2Cl_4 are ubiquitous at their measurable concentrations. The other compounds may not always be present at their measurable

Figure 14

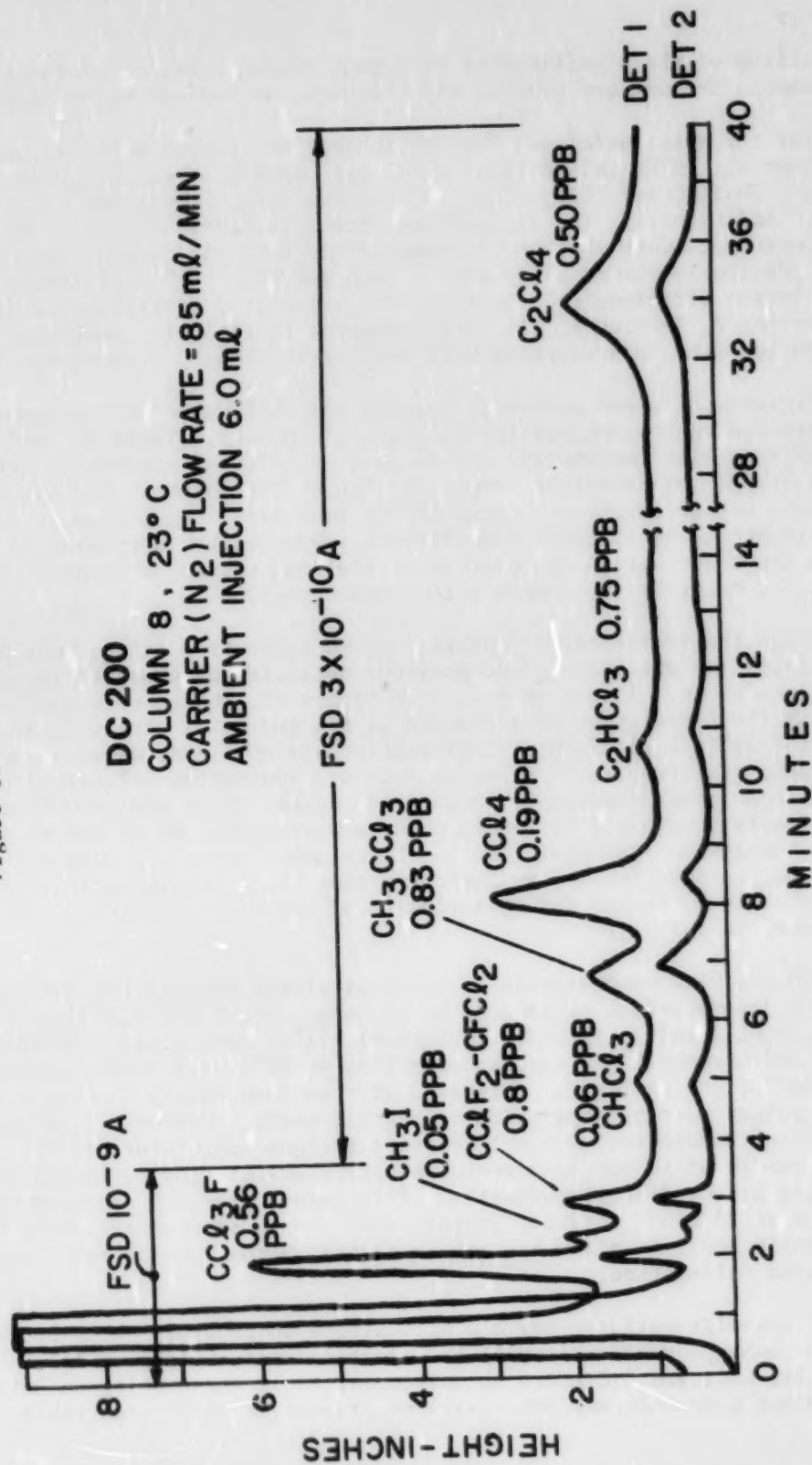


Figure 15

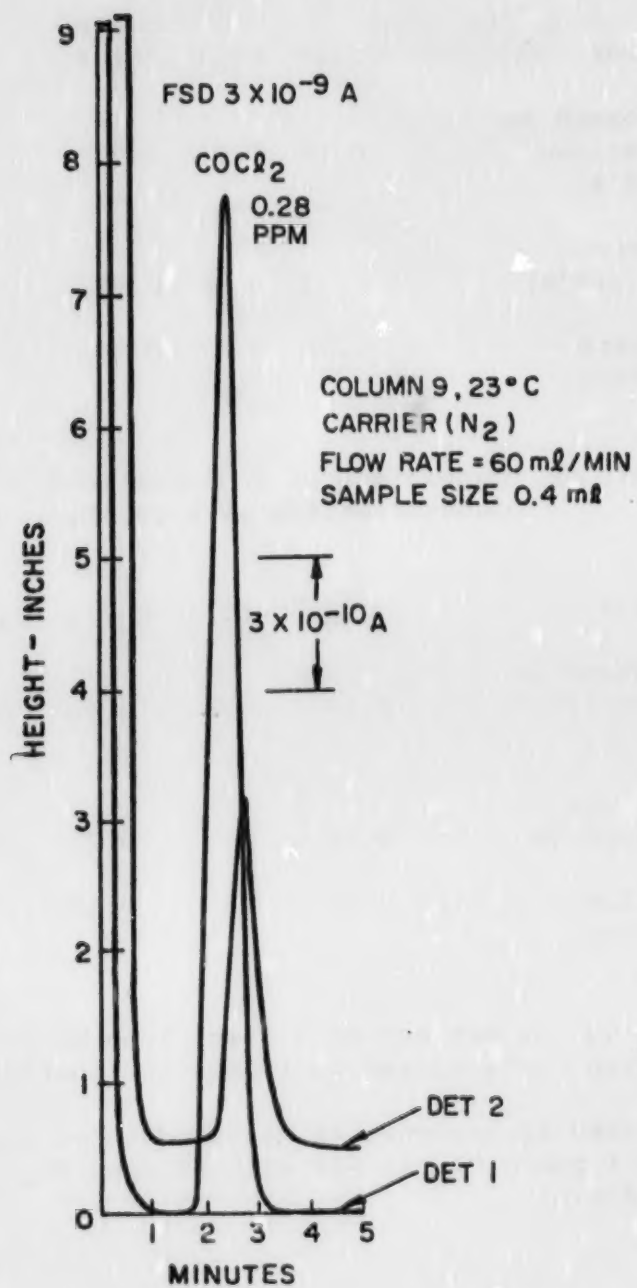


Table 6A. Comparison of Coulometrically Calculated Concentrations with Calibration Standards

Compounds	CCl_3F	CH_3I	$\text{CCl}_2\text{F}-\text{CCl}_2\text{F}$	CHCl_3	CH_3CCl_3
Conc. based on Calibrations (ppb's)	0.56	0.05	0.80	0.06	0.83
Coulometric Conc. (ppb's)	0.42	0.04	0.38	0.02	0.16
Ionization Efficiency	0.75	0.67	0.30	0.20	0.30

Table 6B. Comparison of Coulometrically Calculated Concentrations with Calibration Standards

Compounds	CCl_4	C_2HCl_3	C_2Cl_4	C_2Cl_4^*	COCl_2^{**}
Conc. based on Calibrations (ppb's)	0.19	0.75	0.50	0.53	280.0
Coulometric Conc. (ppb's)	0.16	--	0.22	0.39	100.0
Ionization Efficiency	0.80	--	0.60	0.60	0.75

* This was determined on a 2 ft. long DC-200 column in which C_2Cl_4 eluted in 13 minutes instead of 33.

** Phosgene is reported as measured in an irradiated mixture at 1 ppm C_2Cl_4 in air with 50 pphm NO_2 (50% RH; $K_1 = 0.4/\text{min}$).

concentrations depending upon localized emissions in the sampling area.

The use of purge gas at low concentrations of solute leads to reduced sensitivity. This is attributable to a decrease in ionization efficiency with increasing flow rate through the EC detector.

The utilization of the ionization efficiency as a confirmatory aid has been demonstrated and further applied to confirm the identity of phosgene in a simulated photochemical smog study and, accordingly, the probably tropospheric synthesis of this compound. Because of its high ionization efficiency (>75%) and instability, the latter making the preparation of calibration mixtures extremely difficult, phosgene and similar reactive strong electron absorbers are excellent candidates for coulometric analysis. Accordingly, for such compounds, new packings and passivation procedures are recommended along with a detailed analysis of sorption kinetics.

The exquisite sensitivity of the EC detector to most of the compounds under study and their wide spectrum of emission patterns and reactivities make them excellent candidates for the study of complex atmospheric phenomena. The methods and data presented here should find wide application in studies involving point and multisource diffusion modeling, transport of large scale air masses, photochemical smog and sea breeze modeling and stratospheric exchange.

5.2 Gas Phase Coulometry

Under optimum conditions of near 100% ionization in an electron capture (EC) detector, strongly electron absorbing compounds produce a response of such great sensitivity that femtogram (10^{-15} g) analysis has been suggested⁽¹⁸¹⁾. In this study a coulometric gas chromatographic method of analysis based on gas phase electron absorption has been evaluated and used for measuring the ambient concentrations of several such compounds. Developed by Lovelock⁽¹⁸²⁾, this method is based on a 1:1 equivalency at 100% ionization between the number of solute molecules in a carrier stream to the number of electrons absorbed by them in the EC detector. Accordingly, the solute concentration can be calculated directly from the number of electrons absorbed. At ionization efficiency of less than 100% the use of two identical detectors in series enables one to determine the fractional ionizations in the EC detector and thereby maintain the absolute nature of analysis by correcting for the unionized molecules. A further modification of gas phase coulometry, for use with reactive compounds which undergo decomposition on the gas chromatographic columns, has been developed by us. We have termed it "Pulsed Flow Coulometry" and it will be described in section 5.1.3.

When operated coulometrically at 100% ionization efficiency an EC detector is at its maximum sensitivity since all solute molecules are "counted." Since the method is absolute, sources of mixing and contamination errors inherent in the preparation of extremely dilute calibration mixtures are

precluded. An additional advantage of this mode of operation, particularly in air chemistry studies, is the ability to determine the concentration of an unknown compound and possibly deduce its identity from spatial and temporal distributions of concentrations. Furthermore, rate of thermal electron attachment is an excellent aid for confirmation of identity when used in conjunction with retention data.

5.2.1 Theory -

The theory of gas phase coulometry is as follows: Consider two identical EC detectors in series and let their signals be X_1 and X_2 in coulombs due to an injection of a plug of Q molecules of compound AB. If p is the fractional ionization of AB, at high ionization efficiencies and low solute concentrations one can write:

$$X_1 = pQ \quad (1)$$

$$X_2 = p(Q - pQ) \quad (2)$$

$$p = 1 - X_2/X_1 \quad (3)$$

The gram moles of solute W in the EC detector are therefore from equations 1 and 3.

$$W = \frac{X_1}{96,500 \left(1 - \frac{X_2}{X_1}\right)} \quad (4)$$

For an injection of V ml of sample at t °C, the volumetric mixing ratio C_{AB} is:

$$C_{AB} = \frac{8.5 \times 10^{-4} \times (273+t) (X_1)}{V \left(1 - \frac{X_2}{X_1}\right)} \quad (5)$$

With a recorder the signals X_1 and X_2 are simply the respective chromatogram areas in coulombs.

Ionization efficiencies can theoretically be predicted by considering the EC detector as a stirred tank reactor in which solute molecules undergo pseudo-first-order reactions with electrons present in large excess. For a carrier gas passing through the detector at constant flow rate F_0 simple mass balance gives:

$$\frac{1}{P} = 1 + \frac{F_0}{KV_d} \quad (6)$$

where K is the first order constant and V_d is the detector volume. Verification of the model offers the possibility of determining optimum parameters for coulometric analysis.

5.2.2 Results -

The ionization efficiencies of the compounds studied are listed in Table 7. The functional relationship between peak height and concentration for CCl_4 and CCl_3F are shown in Figure 16. The variations of ionization efficiencies with flow rates are plotted for these compounds over a range of flow rates in Figure 17 and extrapolated from one point through the origin for the other appreciably ionizable compounds (>30%) of Table 7. Concentrations determined coulometrically at intermediate efficiencies of 45% for CCl_3F and 50% for CCl_4 are plotted against known concentrations in Figure 18. Coulometric convergence to actual concentration with increasing ionization efficiency is graphed for these two compounds in Figure 19. A chromatogram for a typical ambient injection in the New Brunswick area is given in Figure 20 and the corresponding coulometrically determined concentrations are reported in Table 8. The chromatograms for the substances exhibiting greater than coulometric response as shown in Table 7 are given in Figure 21 and the effect of varying concentrations on this response is shown in Figure 22 for trans - $\text{CHCl}:\text{CHCl}$.

5.2.3 Discussion -

CCl_4 and CCl_3F were evaluated extensively to verify the linear model assumed in equations 1 and 5. Figure 16 shows that the EC detector is slightly nonlinear over the concentration range studied. With convenient sample size (3-10 ml), this range includes typical to three times ambient concentrations. Clearly, the profiles approach linearity at very low concentrations and would appear to limit accurate coulometric analysis to this concentration regime. Reference to Figure 18 shows, however, for at least CCl_4 and CCl_3F this is not the case. The concentrations calculated with equation 5 are in fact linear with the standard concentrations. This unsuspected result was due to a decrease in ionization efficiency with increasing concentration. The practical consideration here is that by operating coulometrically with two detectors, errors due to non-linearity of a single EC detector were offset over the entire concentration range studied. This behavior is attributed to a complex functional relationship between response, concentration, and ionization efficiency. Qualitatively, this can be explained by considering a non-linear response, suggested by Figure 16, of the type

$$X_1 = pQ - m p^2 Q^2 \quad (7)$$

where m is a constant. Factoring equation 7

$$X_1 = pQ(1 - mpQ) \text{ where } [mpQ] \ll 1 \quad (8)$$

Similarly, the signal in the second detector is

$$X_2 = p(Q - pQ)(1 - mp(Q - pQ)) \quad (9)$$

Defining a detector coulomb efficiency E as the fractional change in

Table 7. Ionization Efficiencies^a

Compound	Ionization Efficiency
CCl_4	0.90
SF_6	0.85 ^b
CCl_3F	0.84
CBrF_2 - CBrF_2	0.70
$\text{CCl}_2=\text{CCl}_2$	0.69
CH_3I	0.63
CCl_2F_2	0.33
CH_3-CCl_3	0.20
$\text{CCl}_2\text{F}-\text{CClF}_2$	0.10
CHCl_3	0.06
$\text{CHCl}=\text{CCl}_2$	0.00
trans- $\text{CHCl}=\text{CHCl}$	< 0.00
$\text{CH}_2=\text{CCl}_2$	< 0.00
CH_2Cl_2	< 0.00

^a Carrier Flow Rate: 33 cm²/min. ^b Porapak Q Column.

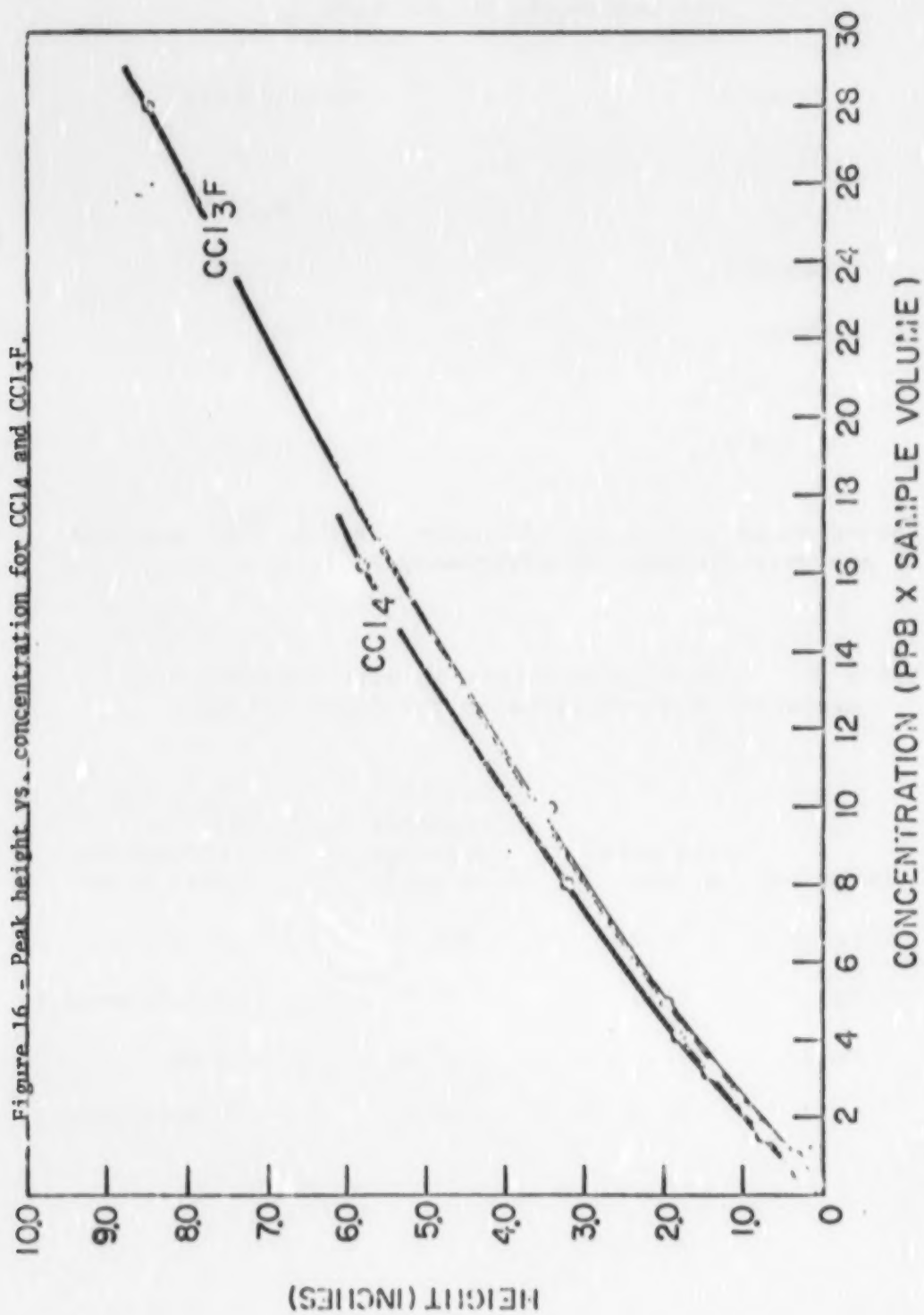
Table 8. Ambient Concentrations of
Coulometrically Determined Compounds in the
New Brunswick, N. J., Area

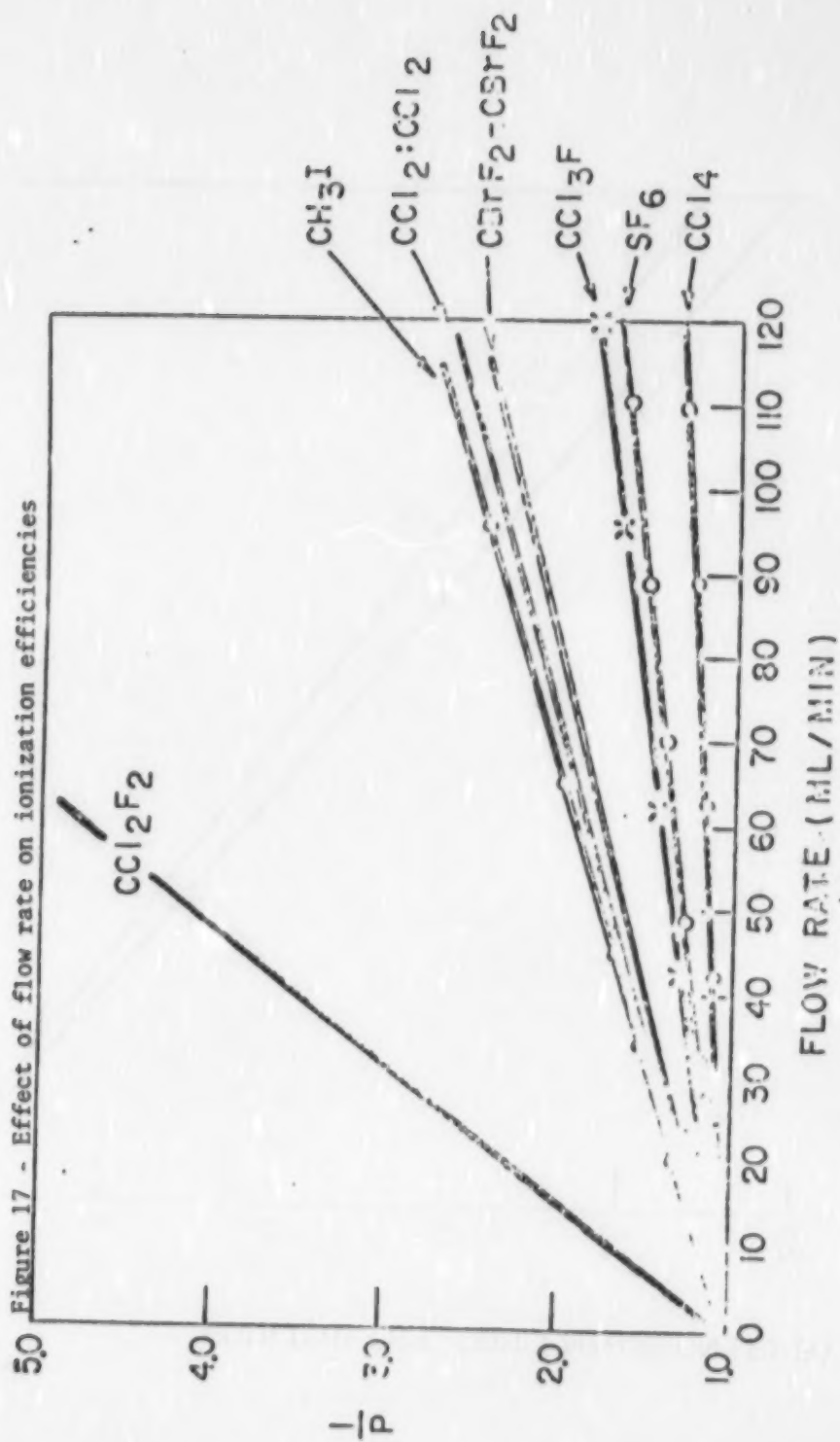
Compound	Concentration ppb
CCl_3F	0.37
CH_3I	0.08
$\text{CH}_3\text{-CCl}_3$	0.27 ^a
CCl_4	0.17
CHCl=CCl_2	 ^b
$\text{CCl}_2\text{=CCl}_2$	0.12

^aBased on an ionization efficiency of 20%. ^bNot amenable to analysis (Ionization efficiency = 0).

Table 9. Effect of Flow Rate on Detector Responses
Responses and Efficiencies for CCl_3F and CH_3I

Compound	Flow rate, ml/min	Detector response coulombs $\times 10^{10}$	Ionization Efficiency
CCl_3F	71.0	209.1	0.73
CCl_3F	11.3	45.0	1.00(approx.)
CH_3I	71.0	135.0	0.60
CH_3I	11.3	16.5	1.00(approx.)





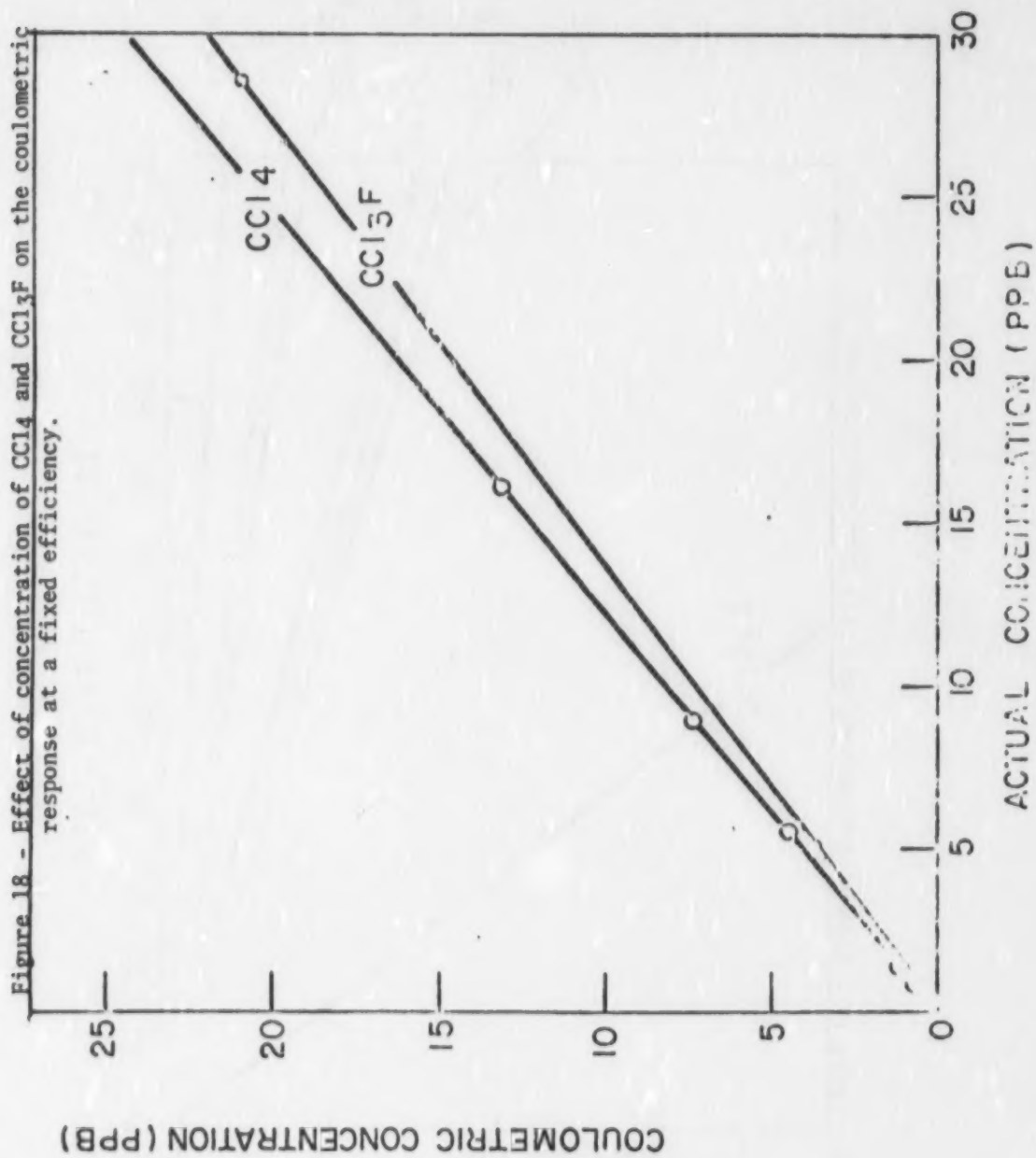
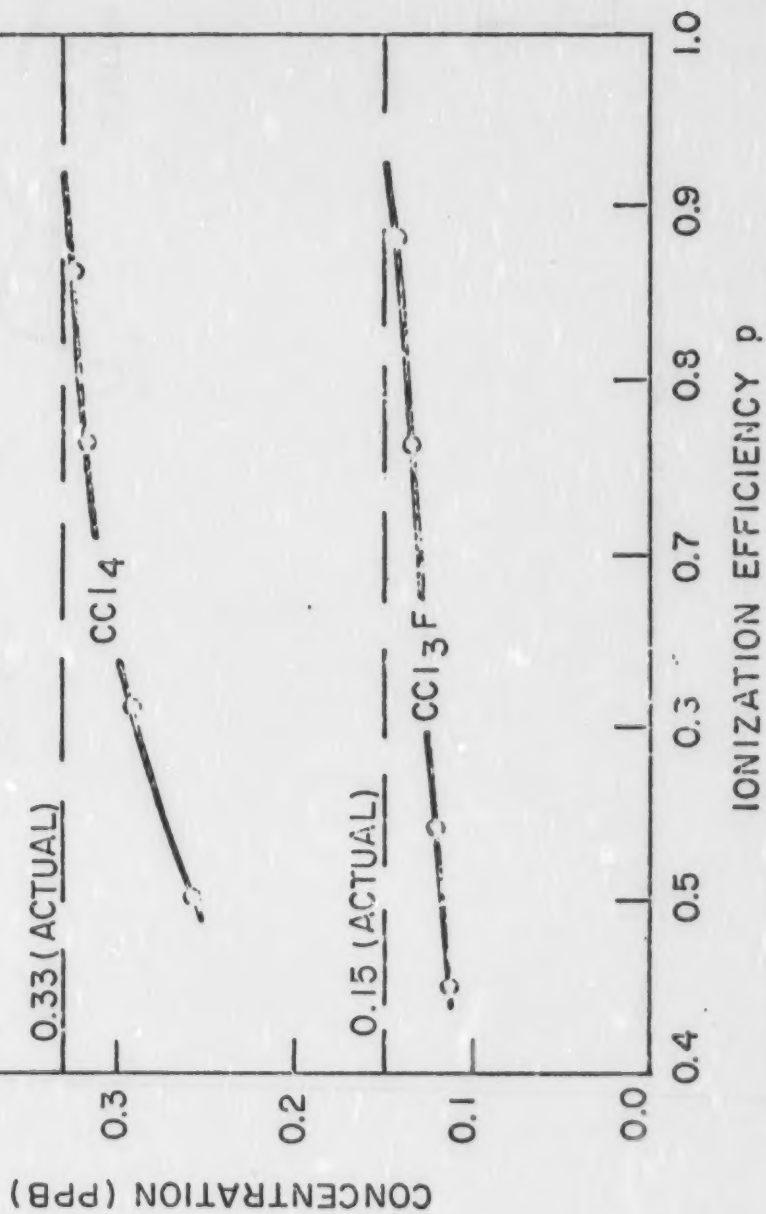


Figure 19 - Convergence of coulometric measurements to actual concentrations as a function of ionization efficiencies.



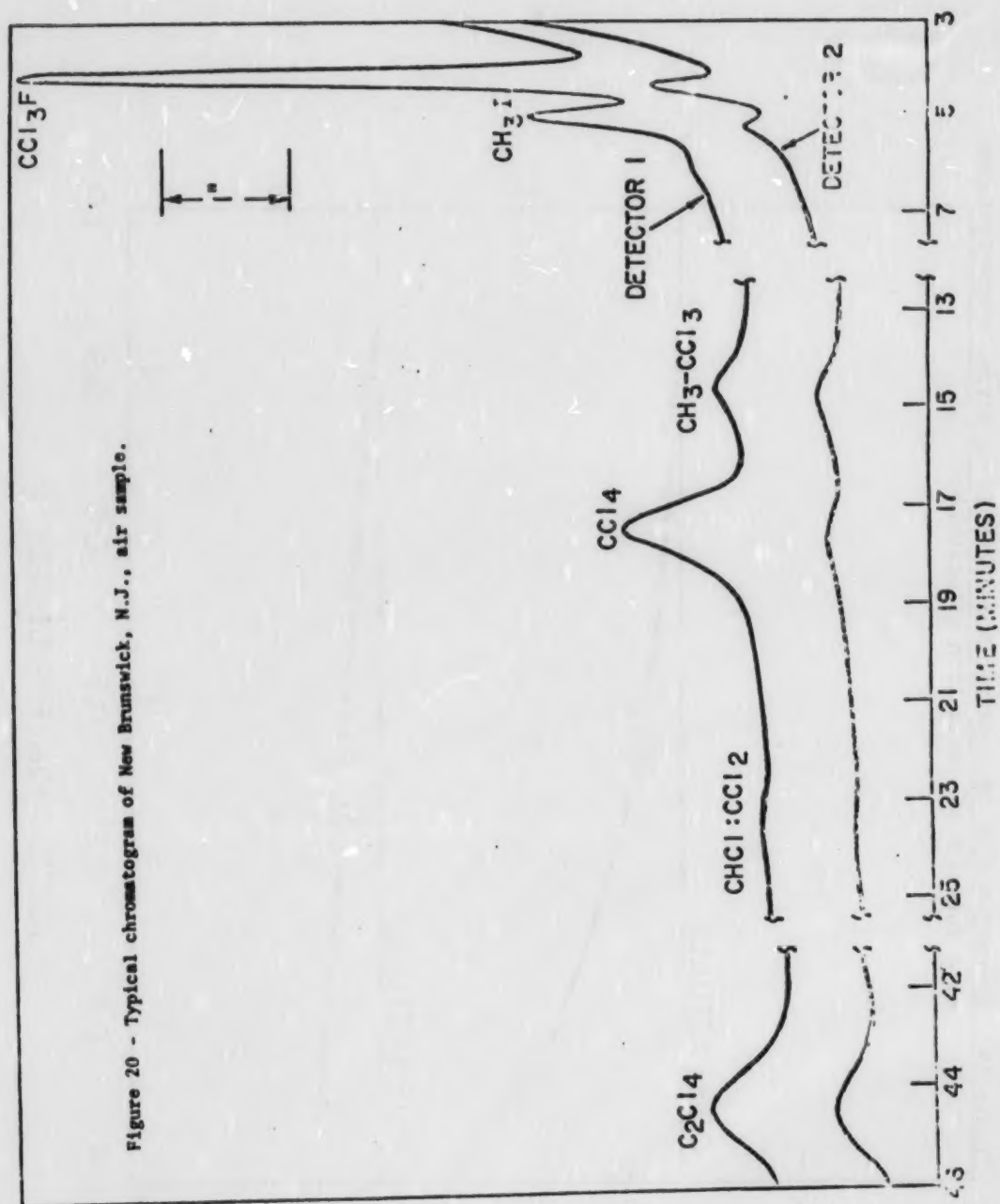
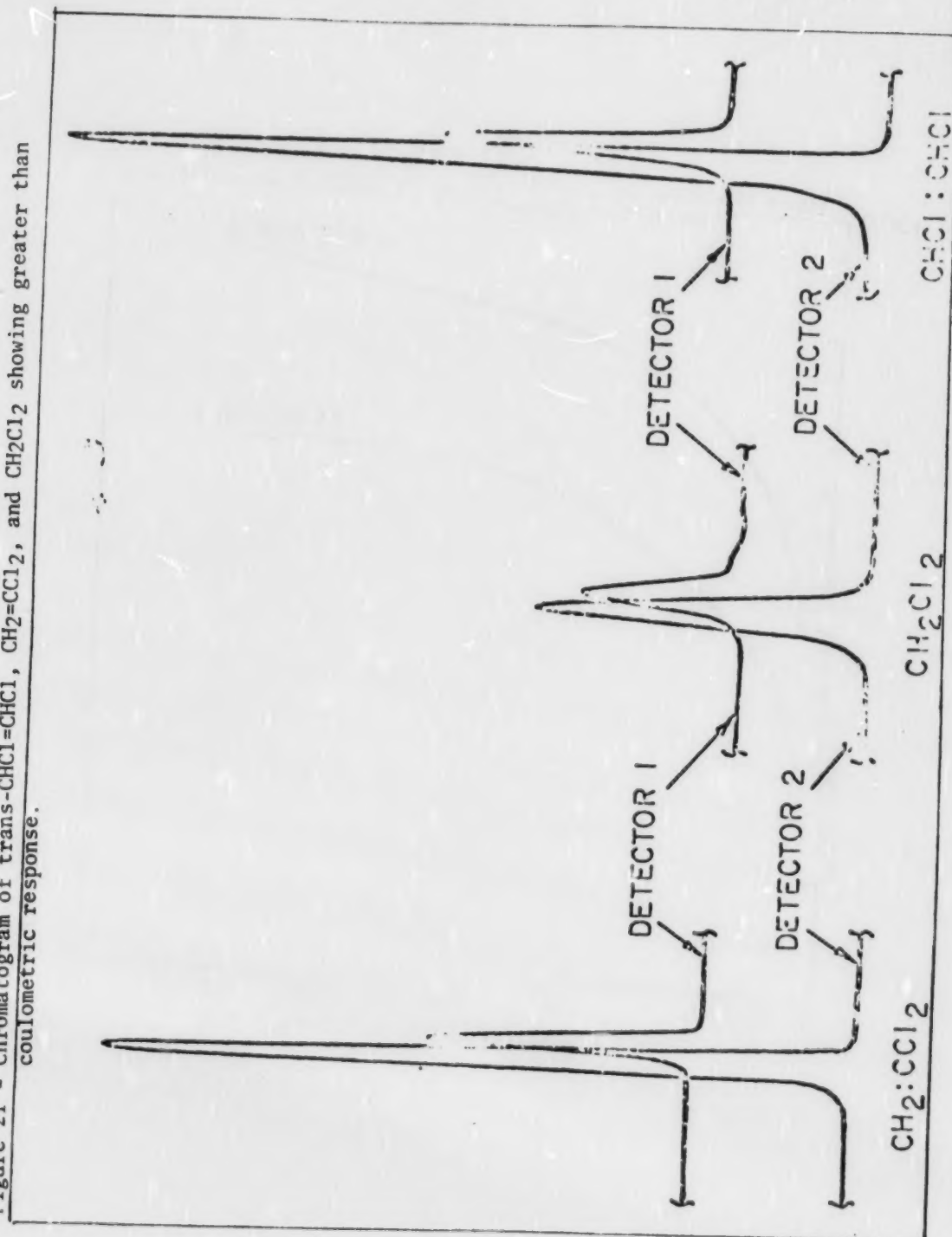
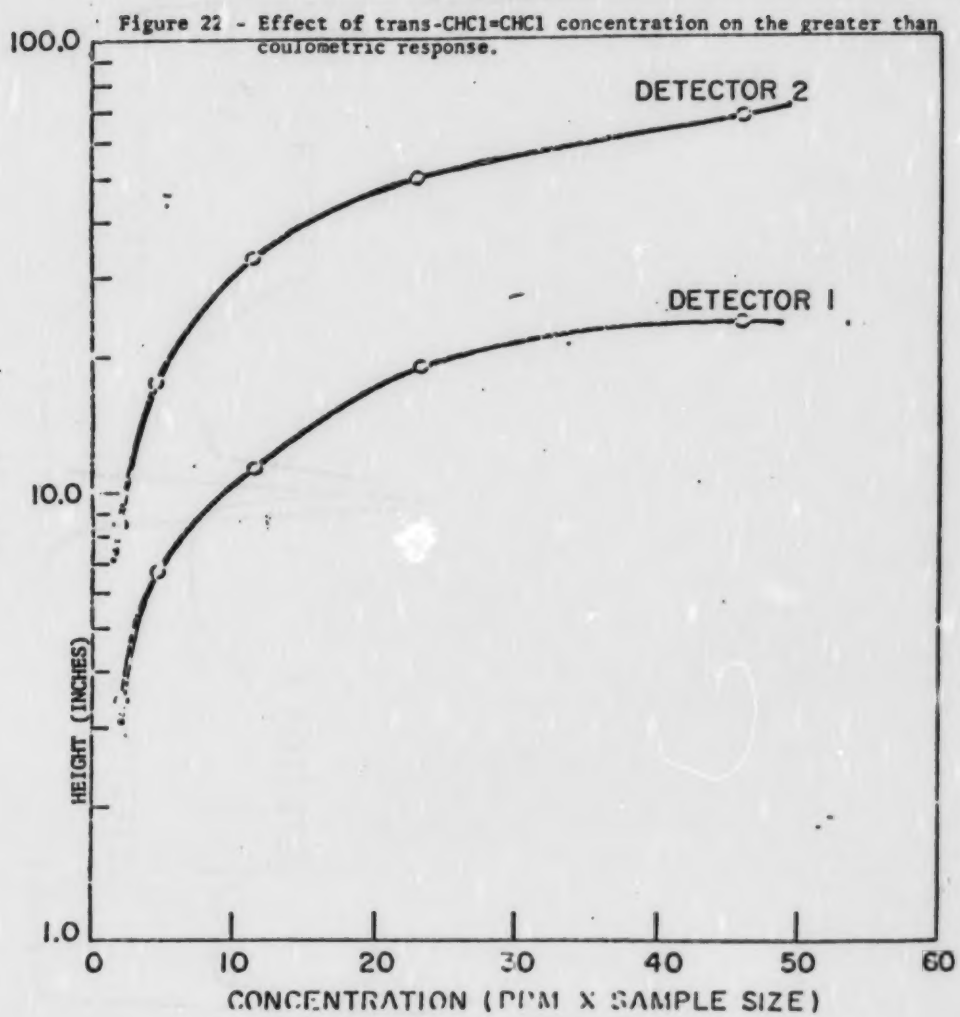


Figure 20 - Typical chromatogram of New Brunswick, N.J., air sample.

Figure 21 - Chromatogram of trans-CHCl=CHCl, CH₂=CCl₂, and CH₂Cl₂ showing greater than coulometric response.





coulombs $X_1 - X_2/X_1$ as distinguished from the definition of p (fractional change in molecules),

$$E = 1 - \frac{X_2}{X_1} \quad (10)$$

By substitution of equations 8 and 9 in 10, one obtains by linearization for the condition $[mpQ] \ll 1$,

$$E = p - mQp^2 (1-p) \quad (11)$$

Clearly, E must always be less than or equal to p . The latter approached E at extremely low concentrations ($Q \rightarrow 0$), under linear conditions ($m \rightarrow 0$), as $p \rightarrow 1$ or a combination thereof. Equations 8 and 11 show a reduction in X_1 and E respectively as Q increases. The linearity seen in Figure 18 is attributed therefore to these effects which help maintain X_1/E as a relative constant and thereby permit an extension of the workable coulometric concentration range. This linearity does not preclude, however, large errors at low efficiencies. The coulometrically determined CCl_3F and CCl_4 concentration range of Figure 18. As the ionization efficiencies approach 100% these errors become negligible as shown in Figure 19. It follows that accurate coulometric analysis requires conditions favoring maximum ionization efficiencies. From our data it seems reasonable that barring irreversible sorption phenomena accuracy greater than 95% should be routinely obtained at ionization efficiencies greater than 90%. Errors of 25% and less can be expected at ionization efficiencies exceeding 50%.

According to equation 6, a plot of the reciprocal efficiency versus flow rate should be linear. This is confirmed for CCl_3F , CCl_4 and CH_3I in Figure 17. The linearity allows one to determine an efficiency at one flow rate and extrapolate it to zero flow rate. This has been done for all appreciably ionizable compounds of Table 7. Practically, one can determine with such plots the feasibility and possible errors of using coulometry. A large slope indicates poor efficiency which can only be compensated for by very low flow rates. A small slope allows flexibility in the choice of flow rates. However, although one can theoretically achieve 100% ionization efficiency for an ionizable compound by approaching zero flow rate, such flow rates may be incompatible with practical analysis. Table 9 gives the detector response at two flow rates for CCl_3F and CH_3I . The responses are seen to fall off drastically at the lower flow rate, making the coulometric response invalid. This phenomenon was attributed primarily to increased sorption and spreading in the GC column, which could more than offset the advantage obtained due to increased efficiency. It follows that one can only reduce flow rates as long as GC response remains constant or increases.

Figure 20 is a chromatogram obtained from an injection of 8 ml. of ambient air in the New Brunswick, N.J. area. Identified peaks are CCl_3F , CH_3I , CH_3-CCl_3 , CCl_4 , $CHCl:CCl_2$, and $CCl_2:CCl_2$. The identity of these peaks was not only established by retention data on different packings (SE30, Porapak Q), but also was confirmed by their efficiency or ionization.

This was found to be a highly reliable method of identification since it is extremely unlikely that two compounds will have the same retention times as well as equal ionization efficiencies. Table 8 shows the ambient concentrations of some of the compounds identified in Figure 20.

Hitherto, it has been considered highly unlikely that a greater than coulometric response ($X_1 > X_2$) could be encountered in practice⁽¹⁸²⁾. In this laboratory, $\text{CCl}_2:\text{CH}_2$, trans-CHCl:CHCl and CH_2Cl_2 were found to yield greater than coulometric response as shown in Figure 21. Figure 22 shows that for trans-CHCl:CHCl the response of the second detector is at least 265% greater than that of the first detector. Since such compounds are apparently rare, dual EC detectors in series can be used reliably to confirm their identification. Further, an increase in sensitivity is possible by using the second detector conventionally. Based on the mechanism for electron attachment proposed by Wentworth⁽¹⁸³⁾, the greater than coulometric response is attributed to the products of ionization having greater electron affinities than the reactants.

5.3 Pulse Flow Coulometry

In the course of this study it became evident that certain highly electron absorbing compounds, which otherwise would be prime candidates for analysis by gas phase coulometry, presented real analytical difficulties because of their tendency to undergo decomposition on the gas chromatographic column. An excellent example of this is phosgene, which is one of the strongest known electron absorbers (comparable to carbon tetrachloride).

Previous workers, as indicated below, have reported difficulties with phosgene analysis due to losses on columns. For example, Priestly et al.⁽¹⁷⁰⁾ reported the electron capture (EC) gas chromatographic determination of phosgene in air. Separation was achieved using an aluminum column packed with 30% didecyl phthalate coated on 100/120 mesh GC 22 Super Support. Dahlberg and Kihlman⁽¹⁸⁴⁾ used a similar GC procedure with a stainless steel column packed with 20% DC 200 on Chromosorb W. The column had to be treated with acetyl chloride to preclude unacceptable phosgene losses. A sensitivity of 1 ppb was achieved by both groups. Jeltres et al.⁽¹⁷¹⁾ used an aluminum column packed with 30% diisodecyl phthalate coated on 80/100 mesh Aero Pak for phosgene analysis and reported a sensitivity of 0.2 ppm with the EC detector.

Because phosgene was expected to be an important product in some of our photochemical studies, and because of its potential importance as an air contaminant, efforts were made to improve on the analytical procedures available.

The wet chemical procedures reported in the literature for the determination of phosgene vapor have been reviewed by Kolthoff et al.⁽¹⁸⁵⁾ and Jeltres et al.⁽¹⁷¹⁾. In general, they suffer the typical difficulties associated with wet chemical procedures, namely, lack of specificity,

interferences, losses in sampling lines and the requirement of large samples precluding real time analysis. Furthermore, such methods are often elaborate and require considerable experience for acceptable accuracy.

Because of its reactivity and the problems associated with wet chemical methods, phosgene analysis is best accomplished by on-site GC procedures. The three columns used by Priestly et al.⁽¹⁷⁰⁾, Dahlberg and Kihlman⁽¹⁸⁴⁾ and Jeltres et al.⁽¹⁷¹⁾, based on our experience, require routine calibrations because of the extreme reactivity of phosgene which causes variable column losses, depending on the column's history. Clearly, an absolute method not requiring calibration or suffering from changing column characteristics is desirable. Reported here is an extension of absolute coulometric analysis which empirically corrects for column sorption through the use of pulse flow kinetics. For brevity the method is called pulse flow coulometry (PFC).

5.3.1 Theory -

The theory of PFC is as follows: In the absence of column losses, from equation 1 above we can write

$$C_e \text{ (ppb)} = C_i \text{ (ppb)} = \frac{8.5 \times 10^5 (273 + t) X_1}{V(1 - \frac{X_2}{X_1})} \quad (12)$$

where C_i is the inlet sample concentration, C_e is the exit concentration expressed as the analogous mixing ratio of eluting C to V ml of mixture, and X_1 and X_2 are the respective serial EC detector responses in coulombs. Use of equation 12 leads to accurate analysis only at high ionization efficiencies ($1 - X_2/X_1$) provided no losses take place in the GC column. Reactive compounds such as phosgene, however, exhibit a significant loss in the GC column requiring the novel application of PFC for absolute analysis. In this procedure a pulse of the reactive constituent is studied by coulometric analysis of the exiting constituent to obtain the decay kinetics in the column.

Consider a packed column of length L and cross-sectional area S through which a carrier gas flowing at a velocity u sweeps a slug of a reactive gas mixture, say phosgene in air. For conditions of no axial dispersion, mass balance gives the instantaneous moles of phosgene traversing the column in time and space as,

$$\frac{\partial C}{\partial t} + u \frac{\partial C}{\partial l} + \frac{\partial C^*}{\partial t} = - (r) \quad (13)$$

where r is the rate of reaction of component C in the GC column, C^* is the adsorbed moles of C in equilibrium with the vapor phase, t is the time, and l is the length along the column axis. Assuming first order kinetics and a linear adsorption isotherm one can write:

$$(r) = kC \quad (14)$$

$$C^* = AC \quad (15)$$

where k and A are the first order rate and adsorption constants respectively. Inserting equations 14 and 15 into 13, one gets:

$$\frac{\partial C}{\partial t} + \frac{u}{1+A} \frac{\partial C}{\partial l} = - \frac{C}{1+A} \quad (16)$$

For the present model the following boundary conditions (B.C.'s) are valid:

$$\text{at } t = 0, \quad C = 0 \text{ for } l \geq 0 \quad (i) \quad (1)$$

$$\text{at } l = 0^+, \quad C = \begin{cases} W(t) & \text{for } t \geq 0 \\ 0 & \text{for } t < 0 \end{cases} \quad (ii) \quad (11)$$

The solution to equation 16 with B.C.'s (i) and (ii) is given by Singh et al.⁽⁴⁾:

$$C = W \left(t - \frac{l(1+A)}{u} \right) \exp \left(-\frac{Cl}{u} \right) \quad (17)$$

$$\frac{\text{Weight (or moles) of } C \text{ out of the column}}{\text{Weight (or moles) of } C \text{ in the column}} = \frac{C_e(\text{ppb})}{C_i(\text{ppb})} = \frac{\int_0^\infty C dt}{\int_0^\infty W(t) dt} \quad (18)$$

$$\text{Since } \int_0^\infty W \left(t - \frac{l(1+A)}{u} \right) dt = \int_0^\infty W(t) dt, \quad (19)$$

inserting equations 17 and 19 into 18, it follows that:

$$\frac{C_e}{C_i} = \exp \left(-\frac{kL}{u} \right) = \exp \left(-\frac{kV_c}{F_0} \right) \quad (20)$$

where F_0 (uS) is the carrier gas flow rate and V_c (LS) is the column volume. Equation 20 can be rewritten as:

$$\ln C_e = \ln C_i - \frac{kV_c}{F_0} \quad (21)$$

5.3.2 Results -

Standard samples of phosgene were prepared at several concentrations (10 to 167 ppb), and each sample was injected into the GC at several known

carrier gas flow rates. Equation 12 was used to determine the column exit concentration at each flow rate. A plot of $\ln C_e$ versus $1/F_0$ was made for each standard sample, and the intercept (C_i) was compared with the standard concentration.

Individual dual EC chromatograms of CCl_3F , CCl_4 and $\text{CCl}_2\text{F}-\text{CClF}_2$ are shown in Figure 23 for standard injections of air-halocarbon mixtures prepared with their respective permeation tubes. A comparison of the standard concentrations with the coulometrically determined concentrations for these compounds at their indicated ionization efficiencies is given in Table 10. Figure 24 is a plot of phosgene permeation tube weight versus time. Presented in Figure 25 are chromatograms of replicate injections of a standard phosgene mixture. Figure 26 shows semi-log plots of C_e versus $1/F_0$ for several standard concentrations of phosgene. A used and a freshly conditioned column were employed in these experiments. A comparison of the standard concentrations with those determined by PFC is presented in Table 11. Figures 27 and 28 show the variation of ionization efficiency with flow rate and input sample concentration respectively. Figure 29 is a plot of phosgene decay in a conditioned glass vessel in the presence and absence of water vapor. Also shown in Figure 29 is the dry phosgene decay profile in a ground-glass vessel having a large specific surface area.

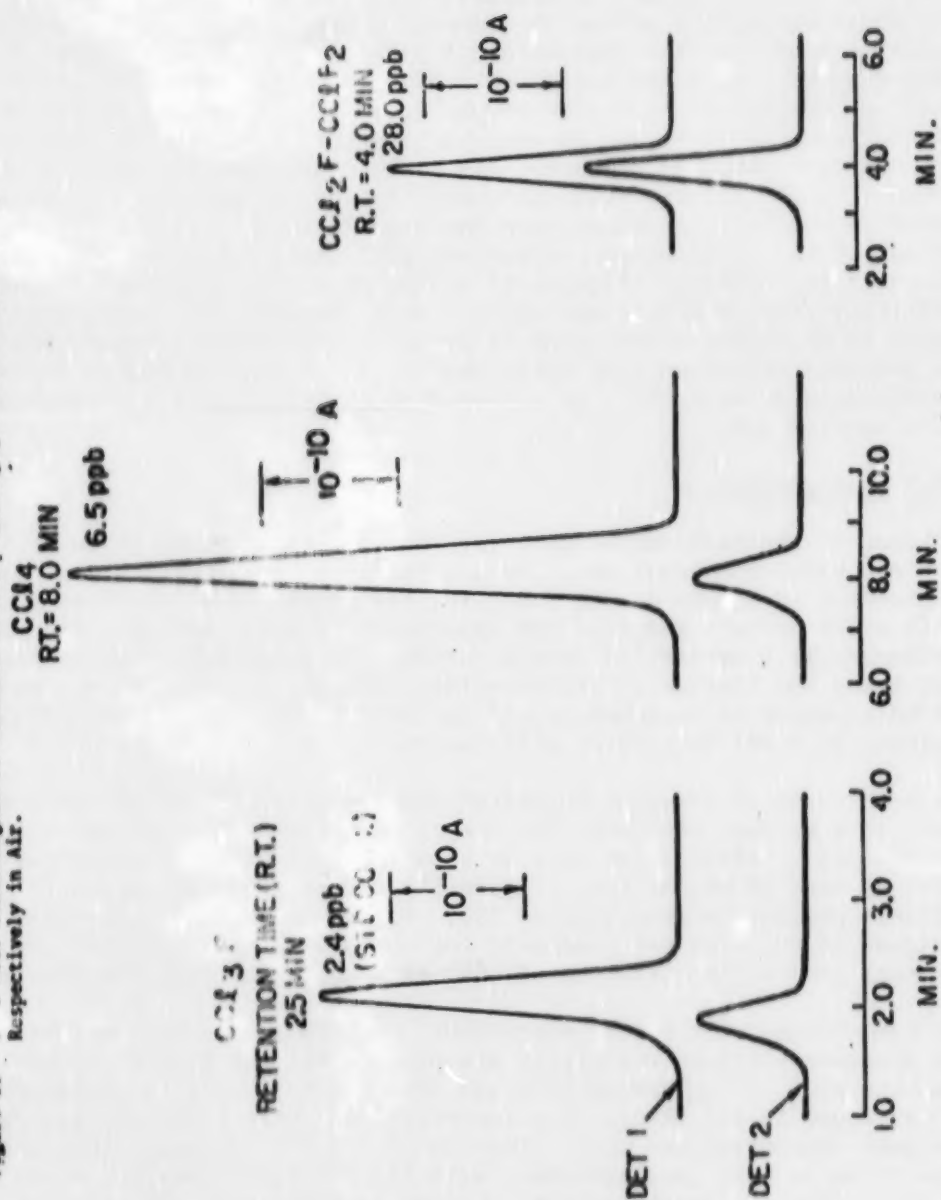
5.3.3 Discussion-

Coulometric analysis can be used for the absolute determination of electron absorbing compounds which do not suffer column losses. This is illustrated in Figure 23 and Table 10, the latter of which shows less than a 15% error between standard ppb injections of CCl_3F and CCl_4 and their coulometrically determined concentrations (equation 12). For compounds exhibiting low ionization efficiencies, however, significant errors can be expected as is demonstrated by the 82% error for $\text{CCl}_2\text{F}-\text{CClF}_2$ analysis at a 28% ionization efficiency.

The reactivity of phosgene suggested the use of a TFE Teflon Permeation tube, as a primary standard, for the dynamic preparation of ppb phosgene-air mixtures. After a few days of conditioning, the tube exhibited a constant rate of weight loss (Figure 24) and provided an extremely reliable phosgene output (Figure 25). Figure 25 further shows that phosgene is an excellent candidate for coulometric analysis because of its high ionization efficiency (>85%) at a convenient carrier flow rate.

The assumptions of a linear adsorption isotherm and first order kinetics for phosgene - column reactivity are proven valid by Figure 26, where semi-log plots of C_e versus $1/F_0$ are shown to be linear (equation 21). As developed in the theory, the intercepts of these lines are the inlet phosgene concentrations (C_i). From Table 11, PFC concentrations are seen to be in very good agreement with the standards (maximum error = 10.2%). This is attributable to the use of ionization efficiencies exceeding 75% and the inherent applicability of the assumed kinetic model. Since the lines are parallel for a given column (Figure 26),

Figure 23 - 1 E.C. Chromatogram of Standard Mixtures of CCl_3F , CCl_4 and CCl_2F_2 respectively in Air.



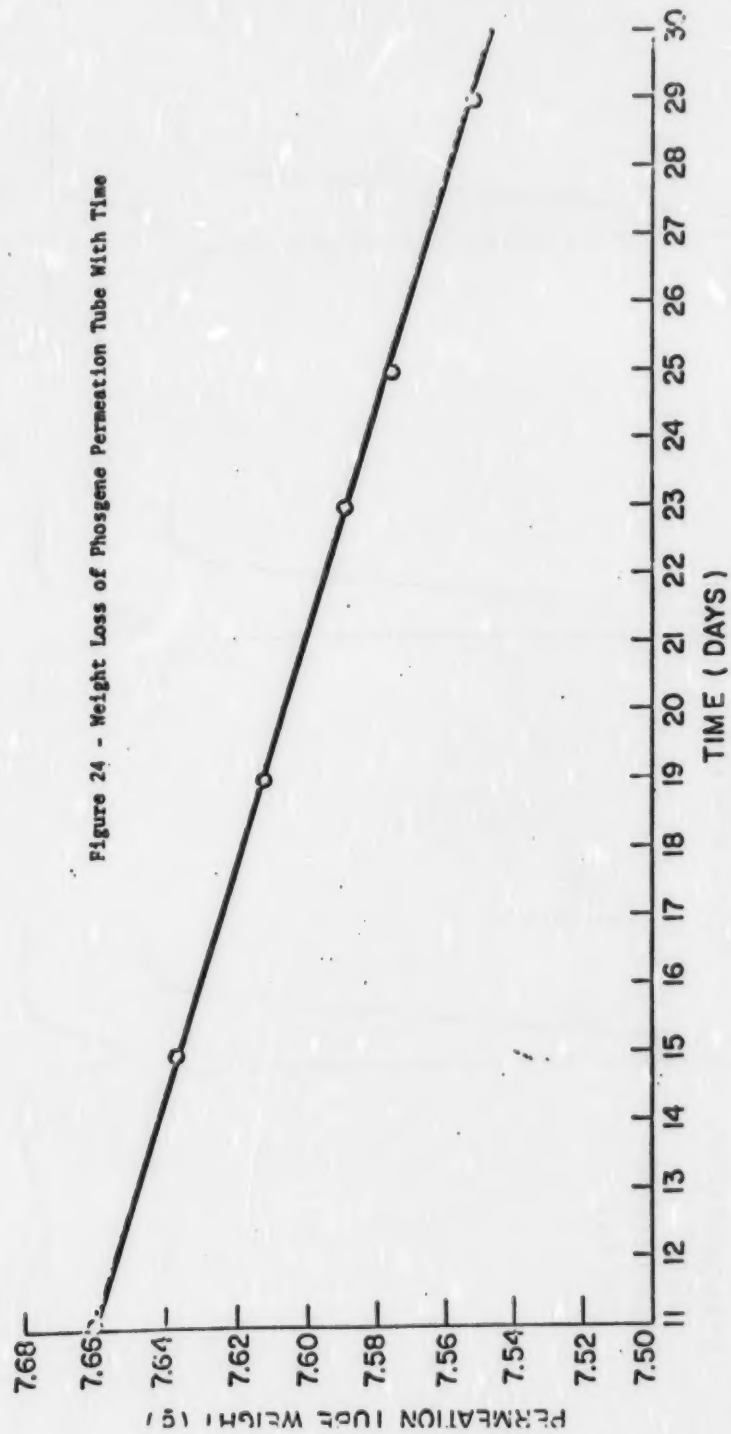


Figure 25 - Dual E.C. Chromatogram of Replicate Injections of a Standard Phosgene Mixture.

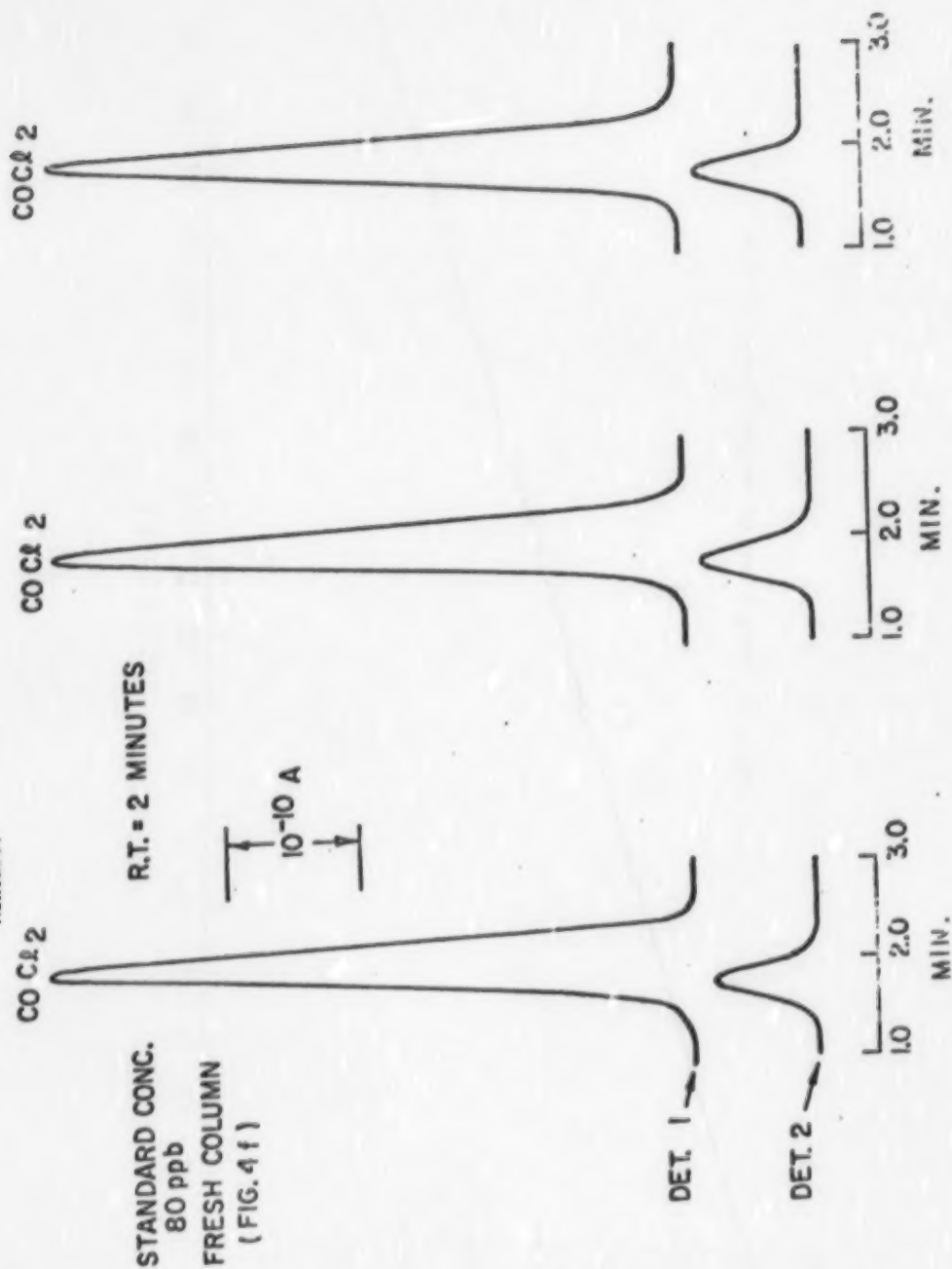
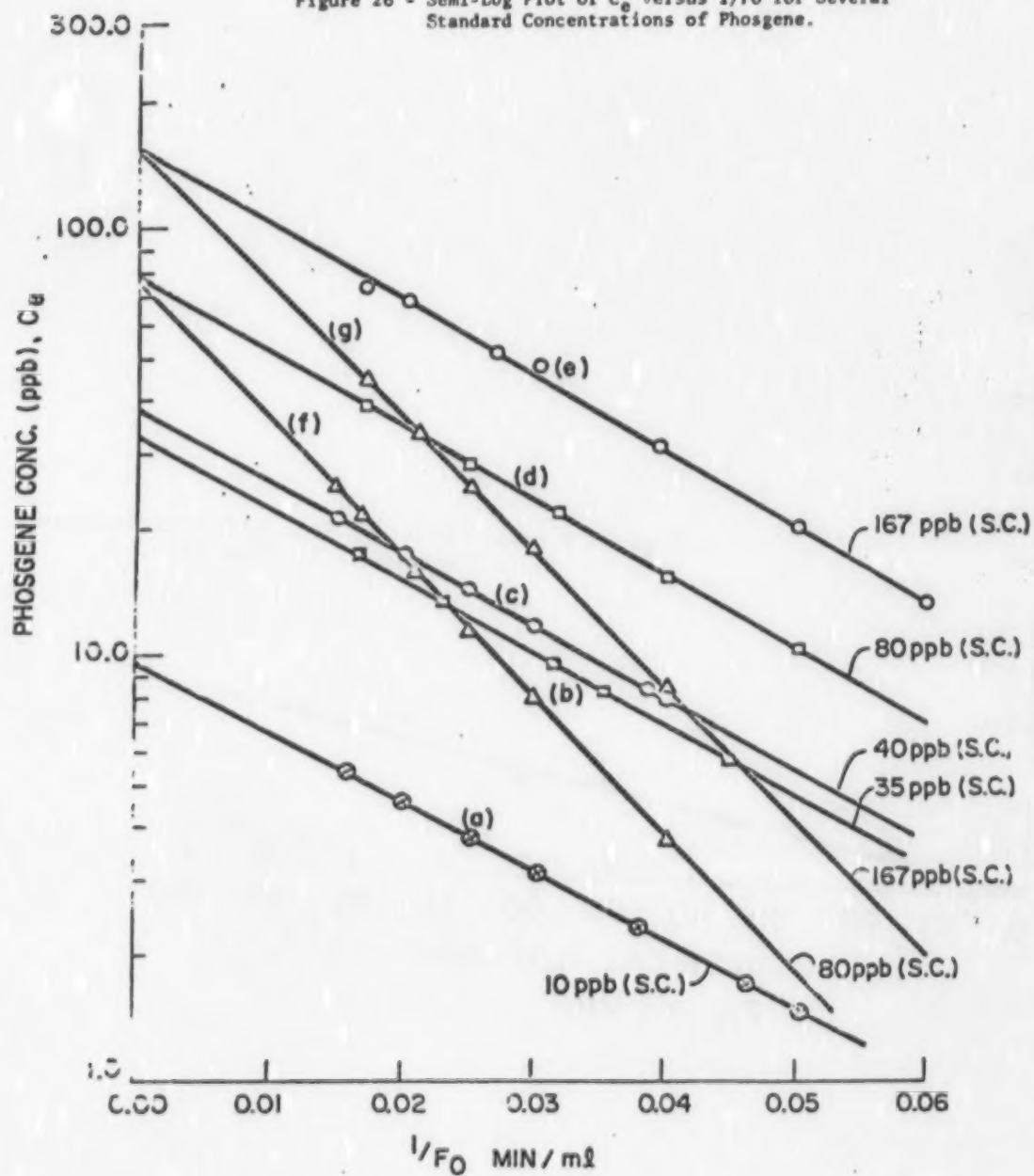


Figure 26 - Semi-Log Plot of C_e versus $1/F_0$ for Several Standard Concentrations of Phosgene.



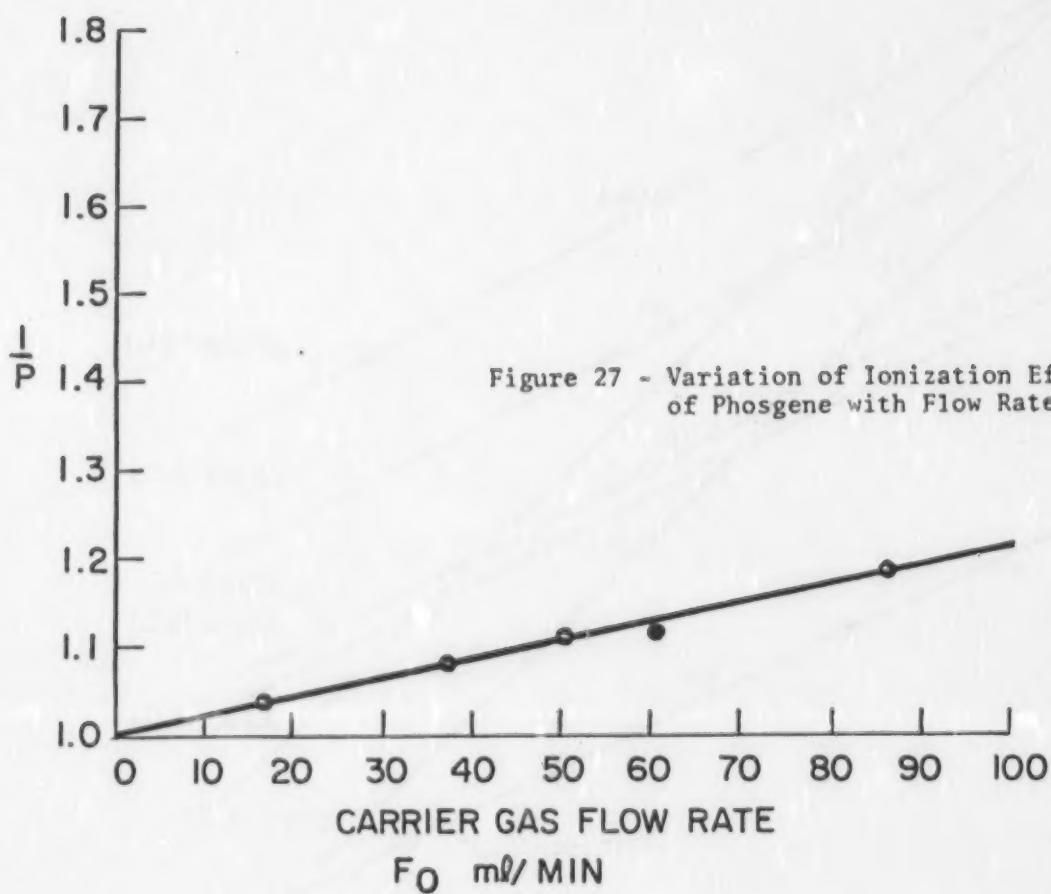


Figure 28 - Variation of Ionization Efficiency of Phosgene with Input Sample Concentration.

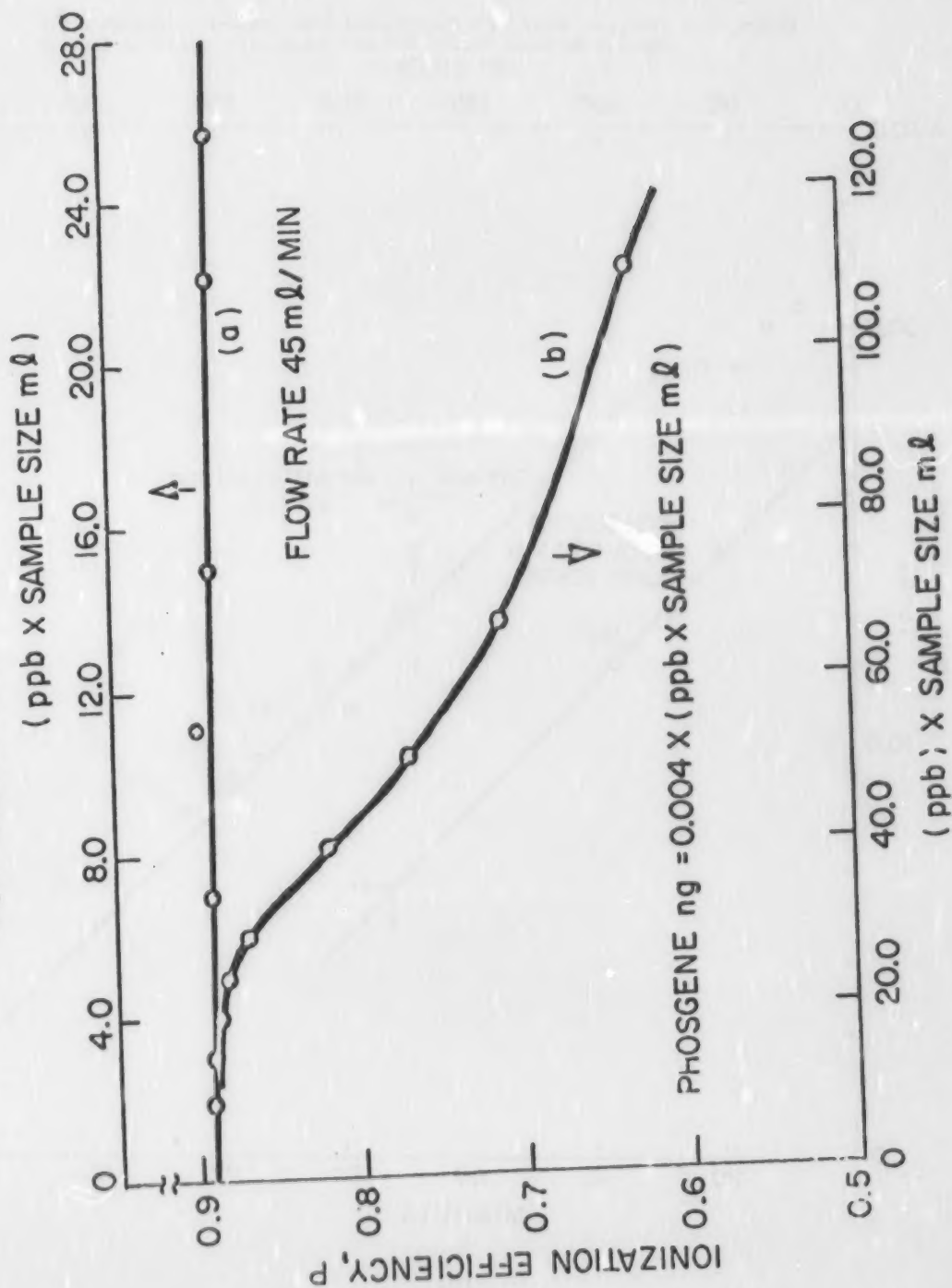


Figure 29 - Phosgene Decay in a Conditioned Glass Vessel in Presence and Absence of Water Vapor, and in Contact with a Ground Surface.

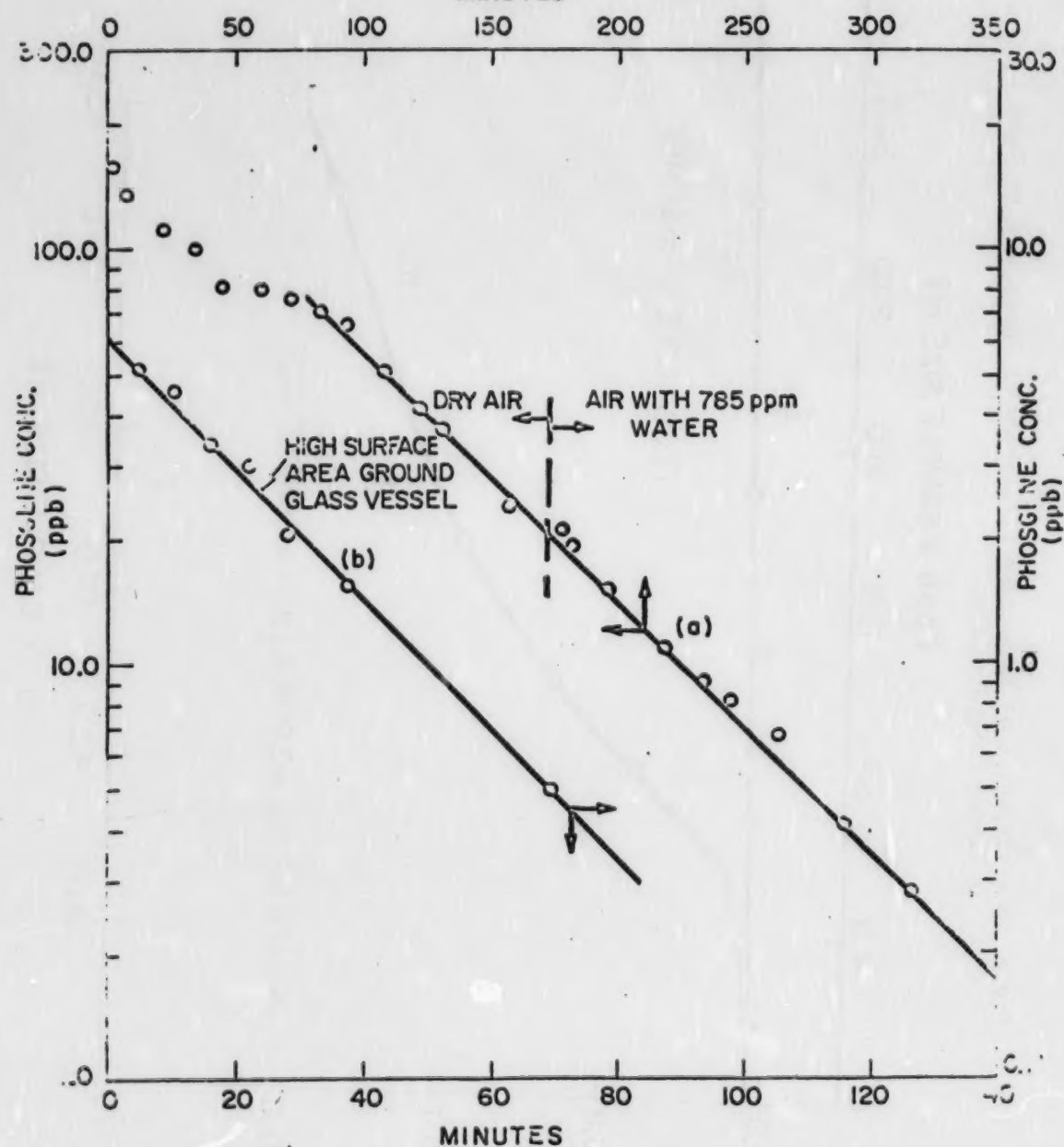


Table 10. Comparison of the Coulometrically Determined Concentrations of CCl_3F , CCl_4 and $\text{CCl}_2\text{F-CClF}_2$ With Permeation Tube Standards.

	Ionization Efficiency p	Standard Concentration (ppb)	Coulometric Concentration (ppb)	% Error
CCl_3F	0.70	2.4	2.1	14.3
CCl_4	0.81	6.5	6.1	6.2
$\text{CCl}_2\text{F-CClF}_2$	0.28	28.0	5.1	81.8

Table 11. Comparison of Standard Phosgene Concentrations with
PFC - Calculated Concentrations

Standard Concentrations (ppb)	Calculated Concentrations (ppb)	% Error	Efficiency Range	Comments
10.0	9.6	4.0	p > 0.85	Used column
35.0	33.0	5.6	p > 0.80	"
40.0	38.0	5.0	"	"
80.00	76.0	5.0	"	"
167.0	150.0	10.2	p > 0.75	"
80.00	76.0	5.0	p > 0.80	Fresh column
167.0	150.0	10.2	p > 0.75	"

once the slope of one of them is determined, analysis is possible by a single injection at one flow rate. The inlet concentration C_i would then be determined as the intercept of the parallel extrapolated line. It is recommended, however, that the slope of an analysis line be routinely checked. The rate constant k may vary gradually with column history as is suggested, in the extreme case, by the different slopes of the lines obtained for the used and the conditioned columns. In conventional GC procedures a change in slope would correspond to a need for a new calibration whereas in PFC, the analogous requirement would be the injection of an unknown sample at a few flow rates. This is substantially simpler than a rigorous calibration, particularly for reactive gases like phosgene.

Since there is evidence^(11,182) that carrier flow rate and solute mass are the major factors governing the ionization efficiency and hence the accuracy of the analysis, the effects of these variables on phosgene ionization efficiency were studied. A linear plot^(11,182) of the reciprocal ionization efficiency versus flow rate (Figure 27) shows that an increase in ionization efficiency can readily be obtained by reducing the carrier gas flow rate. At a given flow rate, however, Figure 28a clearly demonstrates that the ionization efficiency is nearly independent of the input solute mass up to about 0.1 ng. Beyond this the ionization efficiency is seen to fall off, presumably because of the decreasing ratio of electrons to solute molecules (Figure 28b). Consequently, in the regime where solute mass has an effect on the ionization efficiency (>0.1 ng for phosgene), the latter can be increased by a reduction of solute mass as well as of carrier gas flow rate.

Having established the validity of PFC for the absolute determination of phosgene in air, the method was used for a preliminary study of phosgene vapor stability in glass vessels. A 560 ml cylindrical glass vessel (45 cm x 4 cm i.d.) was flushed with a 167 ppb mixture of phosgene in dry air for 60 minutes and was then capped and allowed to stand at 23°C for subsequent analysis. Figure 29a shows the first order decay of phosgene in this system. After three hours, water-saturated air was injected into this vessel by syringe to bring the water vapor concentration to 785 ppm. It is clear from Figure 29a that water had, at best, a minimal effect on phosgene decay. Figure 29b shows a much faster decay of a phosgene-air mixture in a vessel of much higher surface area (ground glass), indicating that the role of water, if any, is manifested in heterogeneous surface reactions. Further, in tropospheric photochemical smog simulation experiments where phosgene was synthesized from C_2Cl_4 in 200 liter Teflon bags⁽⁵⁾, it was found that phosgene concentrations remained stable for periods exceeding 15 hours in the presence of 10,000 ppm of water vapor. We attribute the absence of surface reaction here to the passivation of the walls by photochemical reaction products (CCl_3COCl , $COCl_2$, $HCOC1$, CCl_4 , Cl_2 , HCl , etc.). These results lend support to the observations of Noweir et al.⁽¹⁸⁶⁾ that the importance of phosgene decay by the gas phase phosgene - water reaction has been overemphasized in the literature.

SECTION VI

AMBIENT MEASUREMENTS

Reported here are aerometric halocarbon and SF₆ data obtained during several programmed field studies initiated since March 1973 at various locations in the U.S. which should be representative of a wide gamut of emission patterns and meteorological conditions. The compounds included in these studies were CCl₃F, CCl₂F₂, CH₃CCl₃, CCl₂CCl₂, CCl₄, CHClCCl₂, CH₃I, SF₆, CH₂CHCl, CHCl₃ and CCl₂F-CClF₂. Of these, several were subjected to simulated tropospheric stability studies. Compounds that were found tropospherically stable were tested for possible stratospheric reactivity. Correlations between ozone and halocarbon concentrations monitored at a non-urban location were used for the first time to demonstrate the feasibility and utility of tracing large-scale air masses for elucidation of photochemical smog phenomena.

6.1 Results

Figure 30 shows the locations of the eight monitoring sites. Table 12 presents the complete data for levels of all the above compounds at Seagirt, N.J.; New York, N.Y.; Sandy Hook, N.J.; Wilmington, Del.; Baltimore, Md.; Wilmington, Ohio; and Whiteface Mountain, N.Y. for the dates and times listed during summer and fall, 1974. Also given in the table are data for Bayonne, N.J. taken from March to December, 1973 for all the compounds except SF₆ and vinyl chloride for which analytical procedures had not at that time been perfected. Dashes in this table indicate that analysis of the compound was attempted, but the level was less than the lower limit of detectability.

Table 13 lists the maximum, minimum and mean values observed for these eleven compounds at all eight locations.

Table 14 shows representative levels in urban and rural areas, as well as the halocarbon levels associated with an inversion.

Table 15 lists the daily mean and monitoring period mean ambient levels, and their standard deviations expressed as a percent of the mean. Because of the relative infrequency of monitoring at Bayonne, daily mean values are not listed for this location. Instead, monthly mean values are given in the table. Also indicated in this table are the number of observations at which detectable levels of the compounds were present. It should be noted in using the mean values in Tables 13 and 15 that only those measurements at which detectable levels of compound were observed are included in the mean. In some cases, using this procedure undoubtedly gives a mean value which is too high; however, including zero readings in the mean would, especially in the case of the non-ubiquitous compounds, result in some of the "mean" values being less than the minimum detectable level.

Table 16 shows for each compound at each location the percentage of

MONITORING LOCATIONS

Figure 30

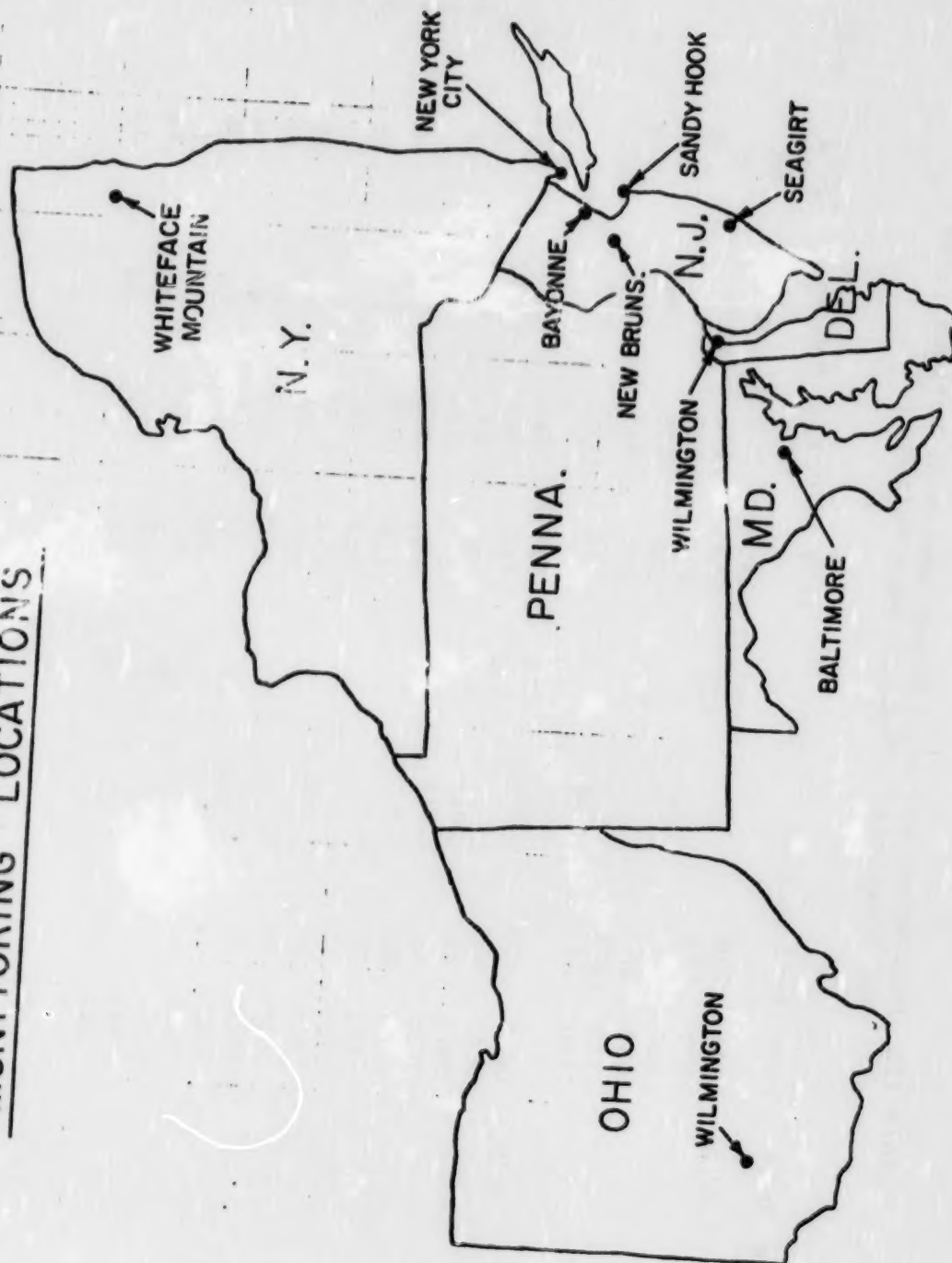


Table 12A. Halocarbon and SF₆ Ambient Levels at Various Times
and Locations: Complete Data Units are ppb

Place	Date	Time	F-11	CH ₃ l	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12
Sea- girt	6/18	1600	.208	-	.06	.146	.207	.28	.88	-
		1800	.117	-	.021	.068	.118	.125	.38	-
		1830	.163	.004	-	.094	.221	-	.338	-
		2030	.25	-	-	.086	.173	.094	.2	-
		2120	.275	-	-	.103	.211	-	.238	-
		2140	.25	.004	-	.103	.221	.094	.275	-
	6/19	0630	.425	.001	.013	.125	.265	.063	.575	-
		0645	.437	-	.006	.118	.275	.125	.575	-
		0815	.27	.013	-	.159	.33	.25	.426	-
		0830	.55	.016	-	.2	.355	.175	.48	.25
		1200	.26	-	-	.103	.252	.1	.4	.38
		1215	.25	-	-	.114	.252	.1	.38	.34
		1300	.175	-	-	.072	.19	.1	.25	.3
		1515	.2	.005	-	.072	.242	.1	.2	.3
		1550	.22	-	-	.075	.252	.1	.19	.3
		1610	.25	-	-	.063	.242	.1	.19	.3
		1625	.18	.005	.06	.044	.19	2.8	.14	.3
		1645	.19	-	-	.053	.227	.06	.26	.3
		1705	.175	-	.06	.06	.227	.1	.1	.3
		1735	.21	-	-	.08	.232	.06	.14	.4
		1845	.175	-	.03	.06	.227	.06	.14	.4

Table 12B. Halocarbon and SF₆ Ambient Levels at Various Times and Locations: Complete Data Units are ppb

Place	Date	Time	F-11	CH ₃ l	CHCl ₃	1,1,1	C ₂ HCl ₃	C ₂ Cl ₄	Vinyl chloride
New York City	6/27	2* 0630	OS ^{1*}	.006	.01	.45	.25	1.45	-
		0715	OS	-	-	.44	.84	2.72	-
		0830	3.35	-	-	.58	.26	-	<10ppb
		0920	3.8	.03	-	.85	.55	9.75	<10ppb
		1100	2.8	-	-	1.5	1.3	-	<10ppb
		1200	1.8	-	-	1.6	1.3	13.3	<10ppb
		1450	.5	-	-	1.24	1.1	3.3	<1ppb
		1650	.6	.01	.48	OS	.93	OS	-
		1645	.64	.015	.29	0.1	1.05	4.0	-
		1715	.6	.009	.07	.125	.75	4.1	-
		1725	OS	.01	-	OS	.7	3.6	-
		1815	.66	.009	-	-	-	9.2	<10ppb
		3* 2100	.8	.005	-	.39	.45	1.4	-
		4* 2140	OS	.005	.01	.295	.47	1.0	<10ppb
		5* 2300	.66	.006	-	.255	.11	1.2	-
6/28	0900	1.9	.003	-	.68	.34	5.1	<10ppb	
	1100	1.1	.003	-	-	.9	6.4	<10ppb	
	1245	OS	.032	.1	.55	.85	10.3	-	
	1330	.9	.003	-	.35	.66	5.5	-	

1* OS = Off Scale
 4* SF₆ = .005, F-12 = 23.75
 2* F113 = .025, F-11 = .5
 3* F-12 = 1.25
 5* SF₆ = .005, F-12 = 1.75
 6* F-12 = .125

Table 12C.

Place	Date	Time	F-11	CH ₃ I	F113	C ₂ F ₃	111T	CCl ₄	C ₂ HCl ₃	CCl ₄	F-12	
Sandy Hook	7/21*	1015	OS	.056	.05	-	.256	.28	.43	.68	-	
		1115	OS	.082	.038	-	.28	.41	.43	.575	-	
		1215	.26	-	-	-	.225	.30	.34	.625	-	
		1235	.29	.087	-	-	.18	.26	-	.44	-	
		1610	.34	.032	-	-	.21	.29	-	1.35	-	
		2045	.21	.044	.175	-	.17	.19	-	.325	-	
		2135	.175	.063	.11	.015	.112	.175	-	.25	-	
		2305	.176	.025	.125	.02	.1	.176	.1	.15	-	
7/3	2*	0105	.176	.035	-	-	.088	.17	-	.15	-	
		0355	.175	.1	-	-	.125	.265	.15	-	-	
		0705	OS	OS	-	-	.20	.49	-	.64	-	
		0744	.25	.16	-	-	.125	.34	-	-	-	
		0915	.53	.15	-	-	.25	OS	.25	.538	-	
		0925	.5	.004	.02	-	.214	.38	-	.32	.4	
		1120	.2	-	-	-	.25	.21	.6	.46	-	
		1135	.275	.08	-	-	.256	.26	.5	.625	.4	
		1507	.4	.019	-	.025	.16	.189	-	-	-	
		1612	.25	.056	-	-	.175	.66	-	.425	-	
		3*	1745	-	-	-	-	-	-	-	.4	
		4*	1910	OS	OS	-	.025	.18	.164	.34	.29	-
			2210	OS	.035	-	-	.243	.252	.25	.375	-
			2310	OS	.063	-	-	.325	.265	.175	.44	-

1* At 1800 on 7/2 F-12 was 2.8, 0.7, 1.4, .45
4* SP₆ = .005
Units are ppb
2* SP₆ = .004
3* SP₆ = .005

Table 12D.

Place	Date	Time	F-11	CH ₃ l	F113	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12	SF ₆		
Sandy Hook	7/4 ^{1*}	0005	.525	.029	-	.15	.176	-	.29	.8	-		
		0110	.75	.05	.025	.15	.164	.25	.375	-	.004		
		0210	.35	-	.025	.12	.20	-	.225	-	-		
		0315								.8	-		
		0340	.46	.037	.05	.15	.22	.34	.29	-	-		
		0600	.475	.023	.025	.156	.164	.34	.25	-	-		
		0930	.35	OS	-	.156	.186	.425	.325	-	-		
		1544	.125	.016	-	.09	.151	-	-	-	-		
		1625	.18	.006	-	.09	.116	-	.15	-	-		
		1645	.225	.005	.012	.112	.164	-	.18	-	.012		
		1730											
		1800							3.2				
		1845							1.8				
	2*	1900	.177	.008	-	.08	.204	-	-	-	-		
		1915	OS	OS	.56	.06	OS	-	.225	1.3	-		
		2015											
		2023	.175	.019	.025	.094	.171	-	.66	-	.004		
		2245	.200	.003	.075	.094	.103	-	.225	-	.004		
		7/5	0035	.12	.025	-	.03	.085	-	.15	-	.004	
			0255	.11	.035	.025	.112	.088	-	-	-	-	
			0355	.10	.024	.025	.037	.078	-	-	-	-	
			3*	1127	OS	.04	-	.056	.093	-	-	-	-
				1600	.138	.028	.025	.10	.103	-	-	-	.004
	1951	.163	.024	-	.048	.086	-	-	-	-			
1* CHCl ₃ = .02			2* CHCl ₃ = .063			3*CHCl ₃ = .016							

Units are ppb

Table 12E.

Place	Date	Time	F-11	CH ₃ l	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12	SF ₆
Wilmington, Del.	7/8	1300	.161	.01	.30	.113	-	-	.4	.004
		1615	.105	.013	.048	.113	-	-	.4	.003
		1*2105	.097	.002	.12	.086	-	.225	-	-
		2*2345	.161	.013	.094	.103	.56	.325	-	-
	7/9	0145	.145	-	.07	.098	-	.075	-	-
		0400	OS	-	.187	.085	.56	-	-	-
		0600	.21	-	.156	.142	.1	.15	-	-
		0835	.17	.01	.13	.131	.175	.15	.4	.006
		1215	.1	.01	.056	.086	-	-	-	.005
		1810								.005
		2115							1.25	
		2135							1.12	
		2148							.5	
		2300	.143	.008	.048	.063	-	.225	-	.004
	7/10	0150	.11	.013	.064	.03	-	-	.7	.004
		1023								.002
		1033								.003
		1220	.095	-	.048	.075	-	-	-	-
		1237	.10	.018	.07	.071	-	.51	-	-
		1450	.10	.008	.03	.071	-	-	-	-

2*Vinyl Cl. = 1500

1* Vinyl Cl = 86

Units are ppb

Table 12F

Place	Date	Time	F-11	CH ₃ I	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12	SF ₆
Balti- more, Md.	7/11	1* 1805	.125	.002	.056	.061	-	.075	.5	.012
		2* 1825	.088	-	.048	.063	-	-	-	.01
		3* 2221	.251	-	.08	.12	-	.25	.5	.003
		2236	.273	-	.08	.095	-	.15	.25	.006
	7/12									.005
		0148	.276	.006	.21	.129	-	-	.8	.006
		0245	.375	.012	.15	.135	-	.184	-	-
		0603	OS	.006	.21	.151	-	.225	.25	.005
		0616	OS	.006	.20	.156	-	.29	.25	.006
		0708	.68	.013	.12	.086	-	.225	-	.007
		1015	.15	.008	.08	.123	-	.15	-	-
		1153	.11	.01	.044	.14	-	-	-	-
		1455	.11	.006	.125	.123	-	.075	.25	-

1* F113 = .025, Vinyl Chloride = 40

2* Vinyl chloride = 37

3* F113 = .038

Units are ppb

Table 12G.

Place	Date	Time	F-11	CH ₃ l	F113	111T	CCl ₄	F-12	SF ₆
Wilming- ton, Ohio	7/16 ^{1*}	1818							
		1831	.110	-	.025	.041	.108		
		1926							0
		1938							0
		2134						0	
	7/17 ^{2*}	2255						.16	
		1020						0	
		1120	.115	.005	.02	.065	.096		
		1436	.260	.016	.010	.265	.154		
		1400	.368	-	.024	.354	.315		
	7/18 ^{3*} ^{4*}	1350	.097	-	.075	.047	.154		0
		1435							
		1505						0	
		1540	.125	-	.009	.047	.181		0
		1645							
	7/21	1710						0	
		1820	.125	-	.009	.047	.154		0
		1915							
		1940						0	
		2015	.115	-	-	-	-		
		2050	.110	-	-	.041	.116		
		2240	.119	-	-	.056	.164		
		2330							0
		2340							0

1* Vinyl Chloride = <10 ppb
 2* At 1316 hrs. SF₆ = 0 and at 1323 SF₆ = 0. At
 1450 hrs. F-12 = 0 and F-12 = 0, at 1455 hrs.
 3* CHCl₃ = .031 and C₂HCl₃ =
 .16, C₂Cl₄ = .425
 4* CHCl₃ = .031, C₂HCl₃ = .16, C₂Cl₄ = .688

Units are ppb

Place	Date	Time	F-11	Table 12H. Fl13	CHCl3	111T	CCl4	C2Cl4	F-12	SF6
Wilming- ton, Ohio	7/22	0225							0	
		0250	.130	-	-	.047	.174	-	-	
		0310	.119	.009	.156	.047	.174	.025	-	
		0530	.116	-	.012	.041	.166	-		
		0625								0
		0640							0	
		0655							.08	
		0730	.119	-	-	.056	.181	-		
		0749	.119	.009	-	.033	.136	-		
		0836							0	
		0842							0	
		0922								
		0932						.08		
		1008	.119	.009	-	.056	.174	-		
		1126	.119	.009	-	.001	.212	-		
		1143 ^{1*}	.130	-	.78	.041	.219	-		
		1243								0
		1259								0
		1350	.156	-	.69	.056	.270	-		0
		1445								
		1519								
		1530							.09	
		1650	.125	.009	1.5	.03	.181	-	.09	
		2139	.130	.009	.012	.056	.391	-		

^{1*} C₂HCl₃ = .52

Units are ppb

		Table 121.									
Place	Date	Time	F-11	CH ₃ l	F113	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12 SF ₆
Wilming- ton, Ohio	7/23	0125	.149	-	-	.031	.081	.370	-	.062	
		0530	.149	-	-	4.78	.056	.272	.63	-	.08
		0920									-
		1130					.065	.144	-	-	
		1139	.119	-	.025	-	.056	.154	-	-	
		1237	.125	.01	.009	-	.281	.237	.08	.175	
		1413	.190	-	.009	-	.144	.269	.25	.2	0
		1523	.190	-	.009	.012					0
		1710									0
		1715									0
	7/24	1805	.175	-	.01	-	.119	.174	.16	.1	
		1845	.187	-	.01	.012	.144	.247	.08	.175	0
		2120									
		2355									
		0045	.119	-	.022	.012	.144	.247	.08	.137	
		0100	.160	.004	.010	.012	.144	.237	.08	.137	.14
		0250									
		0330	.140	.004	-	.031	.281	.355	.25	.312	
		0410	.125	-	.022	.012		.325	.16	.25	
		0425	.097	-	.022	.012	.237	.3	.25	.25	0
		0515									0
		0525									.14
		0550									-
		0600									

Units are ppb

Table 12J.

Place	Date	Time	F-11	F113	CHCl ₃	111T	CCl ₄	C ₂ Cl ₄	F-12 SF ₆
Wilmington, Ohio	7/24	0645	.078	.022	-	.144	.229	.08	0
		0810							.08
		0855							
		1050	.125	.01	-	.104	.229	.062	
		1115	.140	.01	-	.111	.229	.062	
		1315							0
		1323							0
		1359							0
		1420							0
		1*1510	.181	.01	-	.104	.198	-	
		1552	.187	.022	-	.119	.198	-	
		1658							0
		1706							0
		1816							
		1915	.156	.01	.012	.119	.219	.175	.08
		2150							0
		2155							0
		2240							0
		2253							0

1* C₂HCl₃ = .087

Units are ppb

Table 12K.

Place	Date	Time	F-11	F-113	CHCl ₃	111T	CCl ₄	C ₂ Cl ₄	F-12	SF ₆
Wilmington, Ohio	7/25	0005	.375	.022	.012	.095	.229	.1		
		0025	.194	.022	.012	.095	.219	.062		
		0121								0
		0137								0
		0206							.08	
		0215							.08	
		0345	.16	.022	.1	.119	.181	.062		
		0520								0
		0530								0
		0615								
		0635							-	
		0725	.087	.022	.012	.104	.198	.1	.18	
		0745	.119	.035	.012	.104	.229	.137		
		0900								0
		0950								0
		1025							0	
		1040								
		1*1155	.169	.022	-	.111	.219	.137	.08	
		1320								0
		1350								
7/25		1450								0
		2*1515	.169	.01	OS	.09	.277	-		
		1600	.115	.009	-	.081	.198	-		
7/26		3*0202	.156	.01	.012	.095	.277	.06		
		1708	.149	.01	.012	.09	.229	.1		
		2*	C ₂ HCl ₃ = .087		3*	C ₂ HCl ₃ = 0.25				
1*	CH ₃ I = .004									

Units are ppb

Place Date	Time	Table 12L										F-12	SF ₆
		F-11	CH ₃ 1	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	C ₂ Cl ₃	F-12	SF ₆		
White-9/16 face Mt.	1245	.113	.003	.006	.063	.255	.04	.025					
	1330	.108	.003	.006	.045	.252	-						
	1430												
	1510	.150	.003	.006	.051	.267	-	.02		.144			
	1600	.115	-	.006	.038	.244	-						
	1640	.105	-	.01	.045	.222	-						
	1745												
	1810												
	1820	.115	-	.01	.051	.277	.35	.03		.085			
	2100	.130	.002	-	.051	.232	-	.05		.113			
9/17	2245	.115	.003	-	.045	.244	.08	-					
	2355	.125	-	-	.051	.267	-	-					
	0115												
	0125												
	0155	.140	-	.006	.051	.312	-	.02		.113			
	0345	.125	-	.006	.051	.297	-	-		.085			
	0600	.11	-	-	.038	.239	-	-					
	0720	.108	-	-	.043	.222	-	-					
	0750												
	0830												
	0845	.145	-	.006	.051	.305	-	.020		.173			
	0955	.135	-	-	.038	.232	-	.02		.085			
	1015												
	1130	.130	.003	-	.076	.312	-	.09		.085			
	1200	.130	-	.006	.083	.305	.08	.09					
	1300												
	1410	.155	-	.01	.108	.312	.04	-		.113			
	1500	.145	-	-	.102	.312	.08	.13		.07			
	1525												

Units are ppb

Place	Date	Time	Table 12M.						
			F-11	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12 SP ₆
Whiteface Mountain	9/17	1600							
		1625	.170	.025	.127	.305	.02	.11	.113
		1645	.165	-	.134	.282	.13	.19	
		1755							.113
		1810	.150	.01	.121	.312	.13	-	
		2030	.175	.025	.121	.333	.2	-	
		2130							.085
		2150	.165	.006	.108	.312	.04	.120	
		2310							.085
		2330	.130	-	.083	.222	.08	.11	
	9/18	0025							0
		0045	.145		.071	.217	-	.05	
		0100	.125	-	.065	.209	-	.05	
		0245	.115	.006	.045	.204	-	-	
		0400							.085
		0425	.130	.006	.051	.277	-	-	
		0700	.115	.006	.058	.297	-	-	
		1710	OS	-	.032	.257	.08	-	
		0745	.125	.006	.065	.277	-	.05	
		0835							-
		0900							.085

Units are ppb

Place	Date	Time	Table 12N.										F-12		
			F-11	CH ₃ I	F113	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄					
White-face Mt.	9/18	0910	1*												
		0915	.125	-	-	-			.065	.290	-	.07			
		0930	.125	-	-		.006		.065	.290	-	.05			0
		1000													0
		1005													
		1040	.115	-	-		.006		.065	.312	-	.07			
		1100	.08	-	-		-		.053	.232	-	-			
		1115	.130	-	-		-		.051	.290	-	-			
		1335													-
		1350													.085
		1415	.115	-	-		-		.065	.290	-	-			
		1430	.110	-	-		-		.051	.204	-	-			
		1700	.130	-	-		-		.045	.239	-	-			
		2345	.130	-	-		-		.051	.239	-	-			
9/19	1140	.105	-	-		-		.065	.232	-	-				
	1340	.140	-	-		-		.063	.222	-	-	.070			
	1430	.130	-	-		-		.102	.297	.07	-	-			
	1550	.125	-	-		-		.083	.217	.04	.02				.085
	1650														

1* SF₆ = 0

Units are ppb

Table 12 0.

Place	Date	Time	F-11	CH ₃ l	CCl ₄	F-12
Bayonne	3/14	1030	.412	-	.533	-
	1973	1230	.513	-	.597	-
	3/20	1130	0	.038	.0244	.2
		1230	0	.0046	.0033	.25
	3/27	1330	0	.015	-	.22
		1330	.507	.32	.61	.13
	3/29	1430	.407	.202	.52	.1
		1445	-	-	-	.07
	4/2	1330	-	-	-	.09
		1415	-	-	-	.06
	4/3	1330	.137	.0052	0	-
		1430	.119	.0026	0	-
	4/7	1305	.125	.001	0	-
		1400	.11	.002	0	.17
	4/10	1435	0	.0014	0	-
		1200	.0463	.0018	.046	.17
	4/13	1300	0	.0021	0	.32
		1340	0	.0033	0	.95
	4/16	1510	0	.0041	0	-
		1215	.148	.004	.047	.18
	4/20	1315	.24	.005	.099	.3
		1245	0	.0005	.048	-

Units are ppb

Table 12P.

Place	Date	Time	P-11	CH ₃ l	CCl ₄	F-12
Bayonne	4/24	1245	.224	-	-	-
		1330	.224	.019	-	-
		1400	.216	.037	-	-
		1500	-	-	-	.14
	4/30 5/1	1230	0	.0034	-	.3
		1330	0	.0052	.35	.3
		1400	0	.0059	0	-
		1430	0	.0041	0	-
	5/7	1215	.094	.0126	.175	.35
		1330	.173	.0152	.343	.35
		1330	0	.0044	0	-
		1400	.122	.0155	.123	-
	5/14	1445	-	.0199	-	-
		1500	0	-	.057	-
		1330	0	.0089	0	-
		1400	.0629	.006	.0618	.14
	5/18 5/21	1412	.0667	.003	.0618	-
		1420	0	.0209	.0566	-
		1434	.0	.0104	-	-
		1500	0	.0179	0	.1
		1509	0	.0134	0	-
		1515	.0503	.003	0	-
		1520	0	.012	-	-

x Units are ppb

Table 120-

Place	Date	Time	F-11	CH ₃ I	CHCl ₃	11117	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	Fl ₂
Bayonne	5/25	1210	.3	.0458	-	-	-	-	-	-
		1250	1.02	.004	-	-	-	-	-	.10
		1310	.274	.055	-	-	-	-	-	-
		1410	1.1	.0458	-	-	-	-	-	-
		1430	1.3	.0525	-	-	-	-	-	-
	5/30	1440	.124	.059	-	-	-	-	-	.4
		1445	.0347	.0458	-	-	-	-	-	-
		1455	.52	.0196	-	-	-	-	-	-
		1430	.17	.0568	-	-	.283	-	-	-
		1500	.132	.1213	-	-	.283	-	-	-
8/8	5/30	1530	.154	.205	-	-	.38	-	-	-
		1600	.127	.219	-	-	.295	-	-	-
	8/8	0830	.65	.2	.07	1.75	.45	1.75	.31	9.4
		0935	.06	1.75	.11	3.2	1.9	8.8	.61	8.1
		1030	1.7	.62	.23	13.1	.4	3.7	.5	32.8
		1130	1.4	.38	.1	10.5	.45	4.8	.44	25.2
		1230	1.15	4.0	.17	2.25	.28	.7	.7	18.4
	8/14	1330	.7	.25	.17	.62	.28	0	.81	24.9
		0745	.65	.09	4.65	1.75	.44	3.7	7.1	11.5
		0830	1.0	.1	9.3	3.1	.52	3.7	8.2	22.2
		0930	.9	.08	7.2	2.2	.44	2.1	6.1	17.0
		1045	.53	.06	.8	1.6	.5	0	4.5	22.3
		1200	.4	.09	15.0	3.75	.65	1.75	6.0	29.2
		1315	.4	.07	8.0	3.5	.45	0	7.5	18.0
		1430	.25	.04	1.7	.75	.25	1.75	1.5	.60

Units are ppb

Table 12R

Place	Date	Time	F-11	CH ₃ I	F113	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12
Bayonne	8/21	1000	.50	.05	0	0	3.5	.23	0	1.5	17.0
		1130	.42	.04	0	0	.2	.21	0	1.82	17.0
		1200	.93	0	0	0	.1	.14	0	1.1	23.0
		1300	4.8	.06	0	0	.1	.14	0	1.1	19.0
		1400	8.0	.06	0	0	.075	.15	0	.92	19.6
	8/29	1210	.67	.12	1.55	.22	.72	.57	.27	1.25	-
		1300	1.53	.16	.44	.4	1.75	.33	2.17	.91	-
		1330	.85	.12	2.3	.82	.83	.27	1.17	.91	-
		1400	1.08	.1	3.2	.15	1.45	.4	1.5	1.33	-
		1500	.5	.13	1.62	.11	.73	.3	1.17	1.0	-
	9/5	1600	.63	.09	2.22	.09	.83	.25	.75	.61	-
		1225	.3	.05	-	2.22	0	.5	.27	.5	-
		1430	.27	.06	-	.33	.16	.63	.77	.5	-
		1525	.23	.03	-	4.15	0	.55	.22	.27	-
		1635	.2	.1	-	3.1	0	.55	.2	.27	-
	9/11	1730	.18	.03	-	2.0	0	.47	2.3	1.2	-
		1830	.32	.73	-	2.22	0	1.5	3.3	.27	-
		1000	.4	.1	-	0	0	.3	.27	.27	-
		1100	.23	.32	-	0	0	.6	.17	.5	-
		1130	.3	.13	-	0	0	.33	.17	.27	-
	9/25	1200	.3	.32	-	0	0	.65	.17	1.0	-
		1230	.27	.22	-	0	0	.3	.15	.5	-
		1300	.2	.2	-	0	0	.37	.155	0	-
		1215	.8	.07	-	.01	3	.14	.14	1.0	1.4
		1315	.48	.1	-	0	.24	.12	.14	1.4	.9
		1415	.36	.072	-	.19	.24	.13	.76	1.5	.9
		1515	.36	.02	-	0	.2	.11	.76	1.2	1.1
		1615	.64	.06	-	.01	.28	.13	.14	2.4	2.0
		1715	.52	.08	-	.03	.16	.08	0	1.0	1.6
		1815	.42	.07	-	.02	.16	.09	0	1.2	1.7

Units are ppb

Table 12S

Place	Date	Time	F-11	CH ₃ I	F113	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12
Bayonne	10/25	1030	.9	.33	.67	.09	.42	.2	.63	2.5	1.4
		1100	1.2	.8	.4	.16	.4	.5	1.17	1.7	2.4
		1200	.7	.3	.67	.11	.37	.2	1.0	3.0	2.6
		1300	2.25	.62	3.33	.16	.42	.35	.63	2.1	2.0
		1400	.7	.22	1.0	.16	.25	.3	1.17	1.15	3.1
	11/19	1030	6.8	2.2	16.76	.22	.56	.6	2.2	1.96	3.9
		1115	2.92	.88	.36	0	.26	.32	.28	.7	19.6
		1245	3.48	.78	.36	.03	.2	.2	.42	-	47.2
		1330	2.0	.44	.24	.01	.14	.22	.42	.3	43.7
		1415	3.24	.54	4.79	.08	.24	.36	1.4	1.3	40.0
		1500	2.4	.5	2.4	.05	.2	.22	1.4	.46	28.4
	11/27	1000	7.1	1.68	13.3	.8	5.4	3.2	0	2.8	11.3
		1100	8.03	1.4	10.5	.67	6.0	12.0	.45	3.78	9.3
		1200	6.9	2.64	24.0	1.34	14.4	13.68	.36	3.33	20.6
		1300	8.76	3.84	38.2	2.66	6.48	16.2	1.4	3.8	32.7
		1400	6.6	1.68	12.0	.66	5.64	18.0	0	2.1	9.7
		1500	7.1	2.0	16.7	1.2	6.6	10.8	1.8	4.8	22.0
	11/29	1145	2.75	.4	2.0	.1	1.4	4.8	0	.65	1.0
		1245	6.05	1.1	4.0	.1	.42	.63	0	.5	2.4
		1345	3.0	.45	2.5	.068	.35	.45	.2	.56	.3
		1445	1.4	.33	1.5	.068	.28	.33	0	.5	.3
		1545	5.8	.83	4.0	.023	.5	.8	.45	.56	.9
		1645	4.8	1.3	4.8	.25	.78	1.0	0	.5	1.6
	12/6	1115	2.25	.37	.23	.1	.42	.47	0	.91	.1
		1200	2.02	.4	2.0	.22	.25	.33	0	.7	.15
		1330	1.67	.27	1.67	.09	.17	.2	.15	.4	.1
		1415	1.4	.25	1.5	0	.22	.3	0	.56	.1
		1500	5.83	.45	2.33	.023	.28	.3	0	.6	.2

Units are ppb

Table 13A. Maximum and Minimum Halocarbon Levels At Various Locations in The United States. Concentrations (ppb)									
Monitoring Period	Location	Levels	CCl ₃ F	CCl ₂ F ₂	CH ₃ CCl ₃	CCl ₄	CCl ₂ CCl ₂	CHClCCl ₂	
6/18-6/19/74	Seagirt, N.J. (National Guard Base)	Max	0.55	0.38	0.20	0.36	0.88	2.8	
		Min	0.12	0.25	0.044	0.12	0.10	0.05	
		Mean	0.25	0.32	0.10	0.23	0.32	0.26	
6/27-6/28/74	New York, N.Y. (45th & Lexington)	Max	3.8	3.8	1.6	0.37	9.75	1.1	
		Min	0.50	0.5	0.10	0.16	1.0	0.11	
		Mean	1.44	1.5	0.61	0.27	4.5	0.71	
7/2-7/5/74	Sandy Hook, N.J. (Fort Hancock)	Max	0.75	3.2	0.33	0.66	1.4	0.80	
		Min	0.10	0.4	0.03	0.085	0.15	<0.05	
		Mean	0.28	1.2	0.15	0.22	0.39	0.34	
7/8-7/10/74	Delaware City, Del. (Road 448 & Route 72 intersection)	Max	0.21	1.3	0.30	0.14	0.51	0.56	
		Min	0.095	0.4	0.03	0.06	<0.02	<0.05	
		Mean	0.13	0.68	0.10	0.09	0.24	0.35	
7/11-7/12/74	Baltimore, Md. (1701 Poncabird Pass, Ford Holabird area)	Max	0.68	0.8	0.21	0.16	0.29	<0.05	
		Min	0.10	0.25	0.044	0.06	<0.02	<0.05	
		Mean	0.24	0.40	0.12	0.12	0.18	-	
7/16-7/26/74	Wilmington, Ohio (Clinton County Air Force Base)	Max	0.38	0.18	0.35	0.39	0.69	0.63	
		Min	0.078	0.08	0.03	0.096	<0.02	<0.05	
		Mean	0.14	0.11	0.097	0.20	0.15	0.19	
9/16-9/19/74	White Face Mountain New York State	Max	0.18	0.17	0.13	0.33	0.19	0.35	
		Min	0.10	0.085	0.032	0.20	<0.02	<0.05	
		Mean	0.13	0.10	0.067	0.26	0.07	0.10	
3/73-12/73	Bayonne, N.J.	Max	8.8	47	14.4	18	8.2	8.8	
		Min	0.046	0.060	0.075	0.05	0.30	<0.05	
		Mean	1.34	6.27	1.59	1.63	1.63	0.92	

Table 13B. Maximum and Minimum Halocarbon Levels At Various Locations in The United States. Concentrations (ppb).

Monitoring Period	Location	Levels	CH ₃ I	SF ₆	CH ₂ CHCl	CHCl ₃	CCl ₂ F-CClF ₂
6/18-6/19/74	Seagrit, N.J. (National Guard Base)	Max	0.016	NV	<10	0.060	<0.01
		Min	<0.001	NV	<10	<0.01	<0.01
		Mean	0.007	-	-	0.04	<0.01
6/27-6/28/74	New York, N.Y. (45th & Lexington)	Max	0.032	0.005	<10	0.48	0.025
		Min	0.003	<0.001	<10	<0.01	<0.01
		Mean	0.01	0.005	-	0.16	0.025
7/2-7/5/74	Sandy Hook, N.J. (Fort Hancock)	Max	0.16	0.012	<10	0.063	0.56
		Min	0.003	<0.001	<10	<0.01	<0.01
		Mean	0.04	0.005	-	0.03	0.08
7/8-7.10/74	Delaware City, Del. (Road 448 & Route 72 intersection)	Max	0.018	0.006	1500	<0.01	<0.01
		Min	0.002	<0.001	<10	<0.01	<0.01
		Mean	0.01	0.004	790	-	-
7/11-7/12/74	Baltimore, Md. (1701 Poncabird Pass Ford Holabird area)	Max	0.013	0.012	40	<0.01	0.038
		Min	<0.001	<0.001	<10	<0.01	<0.01
		Mean	0.008	0.007	38.5	-	0.03
7/16-7/26/74	Wilmington, Ohio (Clinton County Air Force Base)	Max	0.016	<0.001	NV	4.8	0.075
		Min	<0.001	<0.001	NV	<0.01	<0.01
		Mean	0.007	-	-	0.34	0.016
9/16-9/19/74	White Face Mountain New York State	Max	0.003	<0.001	<10	0.25	<0.01
		Min	<0.001	<0.001	<10	<0.01	<0.01
		Mean	0.003	-	-	0.009	-
3/73-12/73	Bayonne, N.J.	Max	3.8	NV	NV	15	38
		Min	<0.001	NV	NV	<0.01	<0.01
		Mean	0.32	-	-	1.03	4.12

Table 14A. Typical Levels of Halocarbon
Units are ppb

Date & Time	Location	CCl ₃ F	CCl ₂ F ₂	CH ₃ CCl ₃	CCl ₄	CCl ₂ CCl ₂
6/27/74 2300	New York, N.Y. Urban	0.66	1.71	0.28	0.38	1.2
9/17/74 1200	White Face Mountains. N.Y. State (Non-urban)	0.13	0.11	0.083	0.24	0.09
7/2/74 1400	Over Ocean, Sandy Hook, N.J. (3 mi. off shore)	0.23	NV	0.18	0.28	0.73
7/19/74 1300	Seagirt, N.J. -(National Guard Base)	0.18	0.25	0.072	0.19	0.25
7/17/74 1228	Above the Inversion (elevated 5000 ft.) Wilmington, Ohio	0.12	0.070	0.025	0.10	<0.02
7/17/74 1203	Inversion Layer (elevation 1500 ft.) Wilmington, Ohio	8.0	0.95	0.065	2.1	0.73

Table 14B. Typical Levels of Halocarbons
Units are ppb

Date	Location	CHClCCl ₂	CH ₃ I	SF ₆	CH ₂ CHl	CHCl ₃	CCl ₂ F- CClF
6/27/74 2300	New York, N.Y. Urban	0.11	0.0060	0.005	<10.	<0.01	<0.01
9/17/74 1200	White Face Mountains N.Y. State (Non-urban)	<0.02	<0.001	<0.001	<10.	<0.01	<0.01
7/2/74 1400	Over Ocean, Sandy Hook, N.J. (3 mi. off shore)	0.18	0.016	<0.001	<10.	<0.01	0.038
7/19/74 1300	Seagirt, N.J. (National Guard Base)	<0.02	<0.001	NV	<10.	<0.01	<0.01
7/17/74 1228	Above the Inversion (elevated 5000 ft.) Wilmington, Ohio	<0.02	<0.001	<0.001	NV	<0.01	0.13
7/17/74 1203	Inversion Layer (elevated 1500 ft.) Wilmington, Ohio	0.075	<0.001	<0.001	NV	0.12	2.2

Table 15A

Halocarbon and SF6 ambient levels at various times and locations -
 Daily Mean and Monitoring Period Mean Values Units are ppb
 (Parenthesis indicate number of observations at minimum detectable values)

PLACE	DATE	F-11 MEAN	% S.D.	CH ₂ 1 MEAN	% S.D.	F113 MEAN	% S.D.	CHCl ₃ MEAN	% S.D.	111T MEAN	% S.D.
Seagrit	6/18	.21 (6)	29	.004(2) 0				.04 (2)	75	.10 (6)	26
	6/19	.26(15)	42	.008(5) 75				.03 (5)	100	.09(15)	44
	6/18-19	.25(21)	40	.007(7) 71				.04 (7)	50	.10(21)	40
N.Y.C.	6/27	1.47(11)	85	.01(10) 80		.025(1)	0	.17 (5)	124	.65(12)	86
	6/28	1.30 (3)	41	.01 (4) 100				.1 (1)	0	.42 (3)	26
	6/27-28	1.44(14)	78	.01(14) 90		.025(1)	0	.16 (6)	119	.61(15)	79
Sandy Hook	7/2	.24 (6)	29	.06 (7) 33		.1 (5)	60	.02 (2)	20	.2 (8)	40
	7/3	.31 (9)	45	.07(10) 71		.02 (1)	0	.025(2)	0	.2 (13)	35
	7/4	.33(12)	58	.02(10) 100		.1 (8)	190	.04 (2)	75	.12(13)	25
	7/5	.13 (5)	15	.03 (6) 23		.025(3)	0	.016(1)	0	.06 (6)	50
	7/2-5	.28(32)	54	.04(33) 100		.08(17)	163	.03 (7)	67	.15(40)	53
Wilm. Del.	7/8	.13 (4)	23	.01 (4) 50						.14(4)	79
	7/9	.15 (5)	27	.009(3) 11						.11(6)	55
	7/10	.1 (4)	6	.01 (3) 50						.05(4)	40
	7/8-10	.13(13)	28	.01(10) 40						.10(14)	70
Balt Md.	7/11	.18 (4)	50	.002(1) 0		.03 (2)	30			.07 (4)	29
	7/12	.28 (6)	79	.008(8) 38						.14 (8)	43
	7/11-12	.24(10)	75	.008(9) 38		.03 (2)	30			.12(12)	25

Table 133.
Sediment Analysis

PLACE	DATE	Cu		Cd		Pb		Zn		SPG		Vinyl Chloride	
		MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.	MEAN	S.D.
Seagirt	6/18	.19 (6)	20	.15 (4)	60	.39 (6)	64						
	6/19	.25 (15)	16	.29 (15)	241	.3 (15)	53	.32 (12)	16				
	6/18-19	.23 (21)	22	.26 (19)	238	.32 (21)	59	.32 (12)	16				
N.Y.C.	6/27	.25 (14)	16	.72 (14)	54	3.8 (12)	77	1.8 (4)	77	.005 (2)	0		
	6/28	.30 (4)	21	.69 (4)	37	6.8 (4)	35	.13 (1)	0				
	6/27-28	.27 (18)	18	.71 (18)	50	4.5 (16)	67	1.5 (5)	96	.005 (2)	0		
Sandy Hook	7/2	.26 (8)	31	.33 (4)	47	.55 (8)	67	1.34 (4)	79				
	7/3	.30 (12)	50	.36 (7)	63	.41 (10)	32	.4 (3)	0	.005 (3)	20		
	7/4	.17 (12)	18	.34 (4)	21	.29 (11)	48	1.58 (5)	63	.006 (4)	67		
	7/5	.09 (6)	9		.15 (1)	0				.004 (2)	0		
	7/2-5	.22 (38)	55	.34 (15)	50	.39 (30)	62	1.2 (12)	80	.005 (9)	60		
Wilm. Del.	7/8	.1 (4)	10	.56 (1)	0	.28 (2)	25	.4 (2)	0	.004 (2)	0	790 (2)	126
	7/9	.1 (6)	30	.28 (3)	89	.15 (4)	40	.82 (4)	52	.005 (6)	79		
	7/10	.06 (4)	33		.51 (1)	0		.7 (1)	0	.003 (3)	0		
	7/8-10	.09 (14)	33	.35 (4)	71	.24 (7)	58	.68 (7)	53	.004 (11)	102	790 (2)	126
Balt. Md.	7/11	.08 (4)	38		.16 (3)	56		.42 (3)	34	.008 (4)	50	38.5 (2)	5
	7/12	.13 (8)	15		.19 (6)	37		.39 (4)	71	.006 (5)	17		
	7/11-12	.12 (12)	25		.18 (9)	39		.40 (7)	53	.007 (9)	43	38.5 (2)	5

Table 15C.
Units are ppb

PLACE	DATE	F-11 MEAN	% S.D.	CH ₃ I MEAN	% S.D.	F113 MEAN	% S.D.	CHCl ₃ MEAN	% S.D.	111T MEAN	% S.D.
Wilm. Ohio	7/16	.11 (1)	0			.025(1)	0			.041(1)	0
	7/17	.12 (1)	0	.005(1)	0	.02 (1)	0			.065(1)	0
	7/18	.31 (2)	26	0	0	.02 (2)	50	.031(2)	0	.31 (2)	19
	7/21	.12 (6)	8			.03 (3)	133			.05 (5)	10
	7/22	.13(11)	8			.009(6)	0	.51 (6)	109	.05(11)	20
	7/23	.16 (8)	19	.01 (1) 0		.01 (6)	60	1.2 (4)	197	.12 (8)	75
	7/24	.14(11)	21	.004(2) 0		.02(10)	30	.014(6)	64	.15(10)	40
	7/25	.17 (8)	53	.004(1) 0		.02 (8)	40	.026(5)	162	.1 (8)	10
	7/26	.15 (1)	0			.01 (1)	0	.012(1)	0	.09 (1)	0
	7/16-26	.14(49)	46	.007(6) 71		.016(38)	81	.34(24)	297	.097(47)	78
White- Face Mt.	9/16	.12 (9)	12	.003(5) 0				.006(6)	50	.04 (9)	50
	9/17	.14(16)	14	.003(1) 0				.009(9)	67	.085(16)	40
	9/18	.12(14)	7					.006(6)	0	.049(16)	40
	9/19	.13 (4)	12							.083 (4)	18
	9/16-19	.13(43)	14	.003(6) 15				.009(21)	78	.067(45)	39
Bayonne	3/73	.28 (7)	85	.12 (6) 120							
	4/73	.11(10)	74	.006(14) 156							
	5/73	.21(18)	162	.04 (30) 146							
	8/73	1.93(24)	128	.36 (23) 111		2.55 (6)	42	2.05(19)	19	2.43 (24)	129
	9/73	.35(19)	39	.15 (19) 115				.75(11)	172	.21 (7)	24
	10/73	1.15 (5)	57	.45 (5) 6		1.21 (5)	100	.14 (5)	25	.37 (5)	2
	11/73	4.95(18)	46	1.28 (18) 73		9.28(17)	104	.46(18)	150	2.77 (18)	140
	12/73	2.63 (5)	69	.35 (5) 25		1.55 (5)	51	.09 (5)	100	.27 (5)	35

Table 15D
Units are ppb

PLACE	DATE	CCl ₄ %			C ₂ HCl ₃ %			C ₂ Cl ₄ %			F-12		
		MEAN	S.D.	%	MEAN	S.D.	%	MEAN	S.D.	%	MEAN	S.D.	%
Wilm. Ohio	7/16	.11	(1)	0							.16	(1)	0
	7/17	.096	(1)	0									
	7/18	.23	(2)	48	.16	(2)	0	.56	(2)	34			
	7/21	.15	(5)	13									
	7/22	.21	(11)	33	.52	(1)	0	.06	(3)	50	.09	(3)	6
	7/23	.23	(8)	35	.24	(5)	96	.14	(5)	43	.08	(1)	0
	7/24	.22	(11)	41	.14	(7)	57	.17	(9)	53	.11	(4)	31
	7/25	.22	(8)	14	.087	(1)	0	.1	(6)	30	.09	(6)	67
	7/26	.23	(1)	0				.1	(1)	0			
	7/16-26	.20	(48)	40	.19	(16)	38	.15	(26)	95	.11	(15)	32
White- Face Mt.	9/16	.21	(9)	38	.16	(3)	44	.025	(5)	56	.11	(3)	27
	9/17	.29	(16)	14	.08	(9)	75	.08	(10)	75	.10	(12)	40
	9/18	.26	(16)	15	.08	(1)	0	.06	(6)	17	.085	(3)	0
	9/19	.24	(4)	17	.06	(2)	33	.04	(6)	100	.085	(1)	0
	9-16-19	.26	(45)	20	.10	(15)	87	.07	(23)	71	.10	(19)	27
	3/73	.38	(6)	75							.16	(7)	44
	4/73	.06	(4)	50							.26	(8)	103
Bayonne	5/73	.14	(12)	96							.29	(7)	38
	8/73	.42	(24)	83	1.66	(16)	126	2.36	(24)	84	18.9	(18)	38
	9/73	.40	(19)	84	.53	(17)	160	.80	(18)	75	1.37	(12)	31
	10/73	.31	(5)	40	.92	(5)	29	2.09	(5)	34	2.3	(5)	28
	11/73	4.66	(18)	134	.6	(12)	117	1.68	(17)	88	16.4	(19)	99
	12/73	.32	(5)	30	.15	(1)	0	.63	(5)	30	.13	(5)	34

Table 16A. Percentages of Analyses in which Each Compound was Detectable

Place	Date	F-11	CH ₃ I	FI13	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12	SF ₆	Vinyl Chloride
Seagrit	6/18	100	33	0	33	100	100	67	100	0	0	0
	6/19	100	33	0	33	100	100	100	100	81	0	0
	6/18-19	100	33	5	33	100	100	90	100	62	0	0
N.Y.C.	6/27	100	67	7	33	93	93	93	87	27	13	0
	6/28	100	100	0	25	75	100	100	100	33	0	0
	6/27-28	100	74	5	32	89	95	95	89	22	11	0
Sandy Hook	7/2	100	88	63	25	100	100	50	100	33	0	0
	7/3	100	88	6	13	100	100	44	63	21	23	0
	7/4	100	92	62	8	100	100	31	85	28	36	0
	7/5	100	100	50	17	100	100	0	17	0	33	0
	7/2-5	100	93	43	18	100	100	38	75	24	24	0
Wilm. Del.	7/8	100	100	0	0	100	100	25	50	50	50	50
	7/9	100	50	0	0	100	100	50	67	40	57	0
	7/10	100	75	0	0	100	100	0	25	17	50	0
	7/8-10	100	71	0	0	100	100	29	50	35	53	17
Balt. Md.	7/11	100	25	50	0	100	100	0	75	75	100	50
	7/12	100	100	0	0	100	100	0	75	50	63	0
	7/11-12	100	75	17	0	100	100	0	75	58	75	17

Table 16B

PLACE	DATE	F-11	CH ₃ I	FI13	CHCl ₃	111T	CCl ₄	C ₂ HCl ₃	C ₂ Cl ₄	F-12	SF ₆
Wilm. Ohio*	7/16	100	0	100	0	100	100	0	0	50	0
	7/17	100	100	100	0	100	100	0	0	0	0
	7/18	100	50	100	100	100	100	100	100	0	0
	7/21	100	0	50	0	83	83	0	0	0	0
	7/22	100	0	55	55	100	100	9	27	38	0
	7/23	100	13	75	50	100	100	63	63	33	0
	7/24	100	18	91	55	100	100	60	82	44	0
	7/25	100	13	100	75	100	100	13	75	75	0
	7/26	100	0	100	100	100	100	0	100	0	0
	7/16/26	100	12	78	51	98	98	32	52	42	0
White-** Face Mt.	9/16	100	56	0	67	100	100	33	56	100	0
	9/17	100	6	0	56	100	100	56	63	100	0
	9/18	100	0	0	38	100	100	6	38	38	0
	9/19	100	0	0	0	100	100	50	50	100	0
	9/16-19	100	13	0	38	100	100	33	51	79	0
Bayonne	3/73	57	100	-	-	-	100	-	-	100	0
	4/73	67	100	-	-	-	33	-	-	100	0
	5/73	60	100	-	-	-	63	-	-	100	0
	8/73	100	96	55	79	100	100	67	100	100	0
	9/73	100	100	-	58	42	100	89	95	100	0
	10/73	100	100	100	100	100	100	100	100	100	0
	11/73	100	100	100	94	100	100	67	100	100	0
	12/73	100	100	100	100	100	100	20	100	100	0

* Vinyl Chloride = 0

** Vinyl Chloride = 0

analyses where detectable levels were observed.

In Table 17 an attempt has been made to quantify the degree of variation of the ambient levels of the eleven compounds measured. For each compound, a "weighted average standard deviation" has been calculated, by summing all the individual location standard deviations with weighting factors proportional to the number of measurements taken at each location. The resulting values are listed in order of increasing "variability."

This data is presented graphically in Figures 31 to 77 to demonstrate more clearly diurnal trends. Table 18 lists aerometric parameters for all times and locations monitored. For purposes of later discussion, some representative atmospheric measurements taken at four of the monitoring locations are graphed together in Figures 78 - 81. The key to symbols and scale factors used in Figures 31 - 81 is given in Table 19.

6.2 Discussion

Because of the need for a halocarbon data base, initial studies were concerned with characterizing the spatial and temporal halocarbon distributions. At all locations and times indicated in Table 13, CCl_3F , CCl_2F_2 , $\text{CH}_3\text{-CCl}_3$ and CCl_4 were always easily measurable. Accordingly, they have been classified as "ubiquitous" for discussion. The minimum detectable concentrations for the analytical methods used to measure the non-ubiquitous compounds studied are given in Tables 13 and 14.

6.2.1 "Ubiquitous" Halocarbons -

The minimum concentrations that have been observed for the ubiquitous halocarbons, CCl_3F , CCl_2F_2 , CH_3CCl_3 and CCl_4 , since June 1973 at the time and locations indicated in Table 13 are 0.046, 0.06, .03 and 0.05 respectively. It is interesting that the values for CCl_3F and CCl_4 are comparable to the reported background concentrations for the two, of 0.05 and 0.06 ppb respectively^(10,13). The minimum CCl_2F_2 concentration of 0.06 is an order of magnitude less than the concentration used by Su and Goldberg⁽¹⁵⁾ to calculate a 30 year residence time for CCl_2F_2 . Their background CCl_2F_2 concentration of 0.7 ppb is inconsistent with cumulative world production data. The integrated worldwide CCl_2F_2 production would give an average background concentration of less than 0.1 ppb.

During extended periods of inversion the ambient concentrations of the ubiquitous halocarbons may attain values as high as 100-500 times their minimum concentrations. For example, the maximum concentrations observed for CCl_3F , CCl_2F_2 , CH_3CCl_3 and CCl_4 during a three day inversion in Bayonne, N.J. were 8.8, 47.0, 9.8 and 18.0 respectively (Table 13).

Table 17. Halocarbons and SF6 in Order of Ambient Variability - Expressed as Weighted Average S.D. for Each Compound*.

CCl ₄	50.6
F-12	50.7
F-11	59.6
SF ₆	66.1
111T	66.5
C ₂ Cl ₄	68.7
F113	95.4
CH ₃ I	96.5
C ₂ HCl ₃	112
CHCl ₃	129

Vinyl chloride: Insufficient data

*Calculated as

$$\frac{\sum \text{S.D.} \times \text{No. of determinations}}{\text{No. of determinations}}$$

Table 18A. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Seagirt	6/18 1974	1300	200	125	0	0	65
		1330	183	60	0	0	63
		1405	145	50	1	0	
		1430	162	68	0	0	
		1500	107	49	1	0	
		1615	136	60	0	0	84
		1715	137	50	0	0	65
		1815	140	43	0	0	87
		1845	130	43	0	0	91
		1930	135	38	0	0	120
		2100	88	55	0	0	110
		2130	82	32	0	0	87
		2200	82	41	0	0	72
		2230	92	40	0	0	
		2300	86		0	0	
		2400	89	35	0	0	
	6/19 1974	615	100	40	0	0	141
		722	51	88	0	0	103
		800	50	80	10	0	84
		840	69	110	5	0	72
		900	85	77	3	0	68
		925	98	80	3	0	72
		1000	115	55	0	0	84
		1030	106	57	3	0	
		1115	96	47	3	0	76

Table 18 B. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NOx (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Seagirt	6/19 1974	1130	92	40	0	0	95
		1135	112		0	0	
		1200	130	31	0	0	110
		1230	129	33	0	0	87
		1300	129	25	0	0	110
		1330	137	22	0	0	125
		1400	128	21	0	0	122
		1430	134	22	0	0	114
		1500	130	22	0	0	95
		1600	108	22	0	0	106
		1700	116	21	0	0	99
		1730	101	27	0	0	76
		1800	107	23	0	0	80

Table 18C. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)
New York City	6/27 1974	620	0	225	55		144
		630	2	90	250	12	148
		700	0	230	230	6	144
		730	0	150	210	10	148
		800	0	220	290	10	133
		835	0	310	330	13	144
		900	0	325	300	10	179
		1000	0	400	250	20	125
		1050	-	275	80	8	152
		1130	1	180	100	10	137
		1200	0	150	100	12	144
		1325	0	200	250	15	171
		1415	0	170	150	20	
		1505	0	200	100	12	53
		1615	0	500	300	9	61
		1645	0	500	800	11	49
		1730	0	300	225	14	61
		1935	0	275	100	18	19
		2035	0	200	350	8	46
		2105	4	320	350	12	
		2135	0	310	45	10	
		2200	1	140	80	10	
	6/28 1974	810	0	400	200	12	
		935	0	375	250	16	65
		1025	0	600	750	15	84

Table 18D. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
New York City	6/28 1974	1050	0	350	200	18	80
		1205	0	450	350	15	68
		1245	0	375	350	20	65

Table 18E Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Sandy Hook	7/2 1974	1130	104	45	2.7	0	65
		1200	109	77	2.8	0	
		1230	99	90	10	0	57
		1300	116	70	2	0	57
		1330	120		3	0	
		1400	125	48	2	0	
		1600	145		0	0	76
		1700	192	50	0	0	68
		1815	157	49	0	0	76
		1900	139	45	0	0	
		2010	107	35	0	0	61
		2100	80	36	2	0	53
		2200	75	29	0	0	65
		2300	50	26	0	0	80
		2400	40	23	0	0	99
	7/3 1974	100	75	19	0	0	99
		200	71	19	0	0	99
		300	64	25	1	2.3	122
		400	65		0	0	
		500	35	52	2	2	167
		600		55	1	0	
		630		66	8	0	
		700		67	8	0	
		735	26	60	7	0	
		800	30	57	7	0	
		830	23	62	12	1	

Table 18F Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)	
Sandy Hook	7/3 1974	900	42	50	9	1		
		930	39	49	3	0		
		1000	46	53	6	0		
		1100	59	52	5	4		
		1200	100	38	4	0		
		1400	100	37	2	0		
		1500	111	37	1.5	0		
		1700	124	41	1.5	0		
		1845	170	47	0	0		
		2005	97	30	1.1	0		
		2105	63	48	0	0	156	
		2200	43	42	0	0	163	
		2300	23	48	0	0	163	
		2400	20	45	0	0		
	7/4	100	5	47	0.5	0	167	
		200	32	44	0	0	152	
		300	28	50	0	0	171	
		400	24	46	0	0	179	
		500	27	36	0	0	179	
		600	15	40	4.5	0	179	
		700	25	42	5.4	0		
		730	20	36	2	0		
		800	50	32	2	0		
		900	64	35	2.2	0		
		1000	94	40	0	0		

Table 18G. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NOx (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Sandy Hook	7/4 1974	1130	126	43	1.5	2	
		1400	131	25	0	0	
		1500	155	51	2.3	1	
		1600	70	47	4	0	
		1700	150	46	0	0	
		1800	180	36	0	0	
		1900	127	30	0	0	
		2000	90	32	0	0.5	
		2115	101	28	0	0	110
		2200	73	25	1	0	
		2300	65	25	0	0	125
		2400	64	28	0	0	
	7/5 1974	100	48	17	0	0	87
		210		19	0	0	72
		300		17	0	0	68
		400	34	16	0	0	49
		500	31	14	0	0	30
		600	32	16	0	0	27
		700	32	16	1.3	0	23
		800	38	16	1.3	0	23
		900	44	17	0.5	0	21
		1000	51	18	0	0	23
		1100	47	24	2.5	0	30
		1200	46	42	4.5	0	
		1300	58	49	7.0	0	38

Table 18H. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Sandy Hook	7/5 1974	1400	93	17	5.0	0	27
		1530	79	35	3.7	0	34
		1600	60	20	0	0	34
		1700			0		23

Table 18I. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)
Wilmington, Delaware	7/8 1974	1500	120	70	5	0	
		1600	110		8	1	42
		1700	100	68	1.7	1	49
		1800	109	50	1.5	0	53
		1900	95	49	1.7	0	53
		2000	95	45	1	.5	61
		2100	72	52	0	1	72
		2200	43	57	0	0	76
		2300	30	68	0	.5	87
		2400	42	40	.5	.5	91
		100	32	35	0	.4	95
		200	27	40	0	0	103
		300	15	42	0	0	106
		400	22	37	0	0	122
		500	9	40	.8	0	103
		600	3	56	7	0	103
		700	16	51	4.5	0	99
		800	55	42	0	0	95
		900	90	29	.2	0	122
		1000	117	34	1.5	0	129
		1100	133	35	2	0	152
		1200	141	24	0	0	133
		1300	155	25	0	0	129
		1400	150	27	0	0	133
		1515		33	.5	0	

Table 18J. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)
Wilmington, Delaware	7/9 1974	1600	185	34	0	0	198
		1705	180	33	0	0	175
		1800	160	25	0	0	171
		1900	115	29	0	0	179
		2000	85	32	0	0	198
		2100	74	27	0	0	194
		2200	92	22	0	0	209
		2300	76	20	0	0	217
		2400	80	23	0	0	209
		108		20	0	0	209
		200	50	22	0	0	205
		300	40	25	0	0	228
		400	45	21	0	0	247
		500	42	22	0	0	239
		600	32	19	0	0	239
	7/10 1974	700	40	20	0	0	274
		800	50	19	.2	0	285
		900	67	19	0	0	293
		1000	77	15	0	0	277
		1100	100	18	0	0	255
		1200	110	20	0	0	232
		1300	118		0	0	224
		1400	125		0	0	217
		1500	117		0	0	194

Table 18K. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Wilmington, Delaware	7/10 1974	1600	130		55	0	186
		1615			10	0	
		1630	112	126	8	3	186
		1700	110	100	4	0	201

Table 18L Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Baltimore, Maryland	7/11 1974	1800	45			0	
		1900	48	67	10	1.5	23
		2000	32	70	9	0	23
		2100	25	65	3	2	23
		2200	9	95	45	2.5	23
		2300	0	100	130	0	30
		2400	0	185	110	2	30
	7/12 1974	100	0	180	80	3	49
		200	0	100	50	1	34
		300	0	122	70	0.5	27
		400	0	155	85	1	27
		500	0	90	40	1	23
		600	0		160	2	42
		700	0	190	90	3	30
		800	5	150	75	2	30
		900	3	65	32	0	34
		1000	35	35	38	0	19
		1100	45	80	70	0	19
		1230	5.5	20	5	0	
		1300	4.5	40	5	0	46
		1400	4	35		0	23
		1500	4	45	25	1	38
		1600	5	80	95	2	57
		1700	4.5	75	55	3	65

Table 18M. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (ug M-3)
Baltimore, Maryland	7/12 1974	1800	3.5	120	130	2	19

Table 18W. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Wilmington, Ohio	7/19 1974	100	118	34	0	0	175
		200	110	39	0	0	179
		300	100	29	0	0	186
		1100	40	34	2.5	0	141
		1200	41	34	2.1	0	141
		1300	55	30	2	0	118
		1400	60	37	3	1	106
		1500	80	40	4.2	1.5	110
		1600	130	44	2.8	2	114
		1700	150	34	.7	1	87
		1200		33	0	2	38
		1300	76	32	0	1	38
		1400	81	20	0	1.5	42
		1500	93	17	0	1.5	42
		1600	100	18	0	0	42
	7/21 1974	1700	100	18	0	0	46
		1800	105	14	0	0.5	46
		1900	100	18	0	1.5	49
		2000	85	18	0	0.5	53
		2050	73	16	0	0	64
		2200	62	33	0	0	
		2300	47	18	0	1	64
		2400	46	26	0	1	64

Table 18-0. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Wilmington, Ohio	7/22 1974	210	48	19	0	1	80
		300	30	21	0	1	84
		400	32	15	0	1	87
		500	40	16	0	1	84
		600	28	23	0	1	91
		700	48	18	0	0.5	87
		800	47	20	0	0.5	91
		900	53	18	0	0.5	95
		1000	70	16	0	0.5	76
		1100	69	17	0	1	72
		1200	85	19	0	1	95
		1300	102	17	0	1	103
		1400	96	19	0	1	114
		1500	95	14	0	1	106
		1600	88	21	0	0.5	103
		1700	76	15	0	0.5	91
		1800	81	13	0	0.5	95
		1900	79	18	0	0.5	103
		2000	66	46	0	1	
		2100	61		0	0.5	
		2200	60	16	0	1	110
		2300	33	23	0	1	137
		100	42	18	0	1	122
		200	50	15	0	0.5	106
		300	31	16	0	1	117

Table 18P. Aerometric Parameters At Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)
Wilmington, Ohio	7/23 1974	400	23	15	0	1	122
		500	19		0	1	110
		600	20	16	0	1	122
		700	18	22	1	1	125
		800	10	33	1	1	135
		900	21	21	0	1	333
		1200	70	21	0	0.5	76
		1300	74	15	0	0.5	91
		1400	79	14	0	1	95
		1515	71	21	0	1	114
		1600	84	17	0	1	125
		1700	77	20	0	1	125
		1800	68	16	0	1	114
		1900	60	15	0	1	129
		2100	50	15	0	1	137
		2200	43	15	0	1.5	145
		2300	40	14	0	1	152
		2400	45	15	0	1	125
	7/24 1974	100	43	14	0	1	133
		200	35	14	0	1.5	137
		300	30	15	0	1.5	145
		400	29	16	0	1.5	145
		500	27	14	0	1.5	175
		600	30	14	0	1	137
		700	26	14	0	1	125

Table 18Q. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Wilmington, Ohio	7/24 1974	800	30	15	0	1	103
		900	50	15	0	1	95
		1100	60	14	0	1	99
		1200	61	11	0	1	110
		1300	70	23	0	1	110
		1400	73	20	0	1	114
		1500	74	16	0	1	110
		1600	80	16	0	1	118
		1700	86	25	0	1	110
		1800	84	51	0	1	110
		1900	85	33	0	1	121
		2000	87	11	0	1.5	125
		2100	91	16	0	1.5	137
		2215	47	21	0	1	137
		2300	50	13	0	1	125
		2400	41	12	0		121
		100	45	12	0	1.5	129
		200	48	12	0	1.5	144
		300	28	11	0	1.5	137
		400	36	11	0	1	148
		500	41	12	0	1	156
		600	31	12	0	0	148
		700	25	16	0	1.5	152
		800	34	14	0	1.5	152
		900	47	12	0	1.5	133
		7/25 1974					

Table 18R. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Wilmington, Ohio	7/25 1974	1000	67	12	0	1	125
		1200	70	19	0	1.5	118
		1300	88	13	0	1	122
		1400	81		0	1	103
		1500	76	17	0	1	107
		1600	86	14	0	1.5	114
		1700	84	13	0	1	118
		1800	95	13	0	1	145
		1855	96	14	0	1.5	167
		2000	85	11	0	1	186
		2100	68	13	0	1	186
		2200	59	14	0	1	178
		2300	54	12	0	1.5	163
		2400	50	16	0	1.5	171
		100	51	13	0	1.5	178
		200	60	11	0	2	175
		300	54	11	0	2	171
		400	46	11	0	1.5	163
		500	52	11	0	1	163
		600	49	11	0	1	160
		700	35	12	0	1	160
		800	32	13	0	1	160
		900	45	13	0	1	156
		1005	59	11	0	1	152

Table 18S. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)
Wilmington, 7/26 Ohio 1974		1100	61	12	0	1	152
		1200	72	13	0	1	156
		1300	91	13	0	1	167
		1400	99	13	0	1	182
		1500	100	13	0	1	198
		1600	100	14	0	1.5	190
		1700	100	13	0	1.5	194
		1800	100	13	0	1.5	194
		1900	92	11	0	1.5	194
		2000	88	12	0	1	190
		2100	71	12	0	1	194
		2200	66	15	0	1	209
		2300	65	14	0	1.5	206
		2400	42	19	0	2	202
7/27 1974		100	52	14	0	2	190
		200	40	11	0	2	190
		300	38	12	0	2	171
		400	20	17	0	1.5	160
		500	25	14	0	1	179
		600	11	12	0	1	137
		700	5	12	0	1	141
		800	8	10	0	1	137
		900	30	12	0	1	125

Table 18T. Aerometric Parameters at Various Times and Locations:

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (ug M-3)
Wilmington, Ohio	7/27 1974	1000	65	16	0	1.5	144
		1200	102	15	0	1	175
		1300	102	15	0	1	171

Table 18U. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates ($\mu\text{g M}^{-3}$)
Whiteface Mountain	9/16 1974	1400	37	21	0		19
		1500	39	20	0		23
		1600	40	5	0		19
		1700	44	6	0		19
		1800	39	5	0		19
		1900	39	3	0		19
		2100	42	5	0		19
		2200	46	4.5	0		23
		2300	47	4.8	0		23
		2400	41	4.8	0		23
	9/17 1974	100	32	4.5	0		23
		200	38	4.5	0		27
		300	38	7.5	0		23
		400	35	5	0		19
		500	34	4.5	0		19
		600	32	4.5	0		19
		700	29	4	0		19
		800	34	4.5	0		23
		900	33	6	0		23
		1000	33	5	0		19
		1100	46	5.5	0		19
		1200	61	5.5	0		15
		1300	62	5.5	0		23
		1400	69	5.5	0		38

Table 18v.

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M ⁻³)
Whiteface Mountain	9/17 1974	1500	70	5.5	0		46
		1600	77	3.5	0		53
		1700	72	6	0		53
		1800	74	6	0		49
		1900	-	-	0		49
		2000	78	6	0		61
		2100	60	5	0		34
		2200	55	4.5	0		27
		2300	42	5.5	0		27
		2400	33	4.5	0		30
	9/18 1974	100	27	4.5	0		8
		200	32	3	0		11
		300	29	2.2	0		11
		400	30	4	0		8
		500	26	8.5	0		8
		600	33	5	0		8
		700	30	4.8	0		
		800	28	4.4	0		
		900	29	3.5	0		
		1000	30	5.5	0		
		1100	24	5	0		
		1300	42	11	0		11
		1400	41	1.5	0		9
		1500	40	2.5	0		9

Table 18W. Aerometric Parameters at Various Times and Locations

Place	Date	Time	O ₃ (ppb)	NO _x (ppb)	NO (ppb)	CO (ppm)	Particulates (µg M-3)
Whiteface Mountain	9/18 1974	1700	42	2.8	0		11
		1800	33	2.2	0		11
		2400	27	2.3	0		15
	9/19 1974	1200	61	6.5	0		57
		1400	60	6.0	0		46
		1500	63	7.0	0		46
		1600	64	6	0		46
		1700	57	5	0		57

TABLE 19A. SCALE FACTORS USED IN FIGURES 31-77

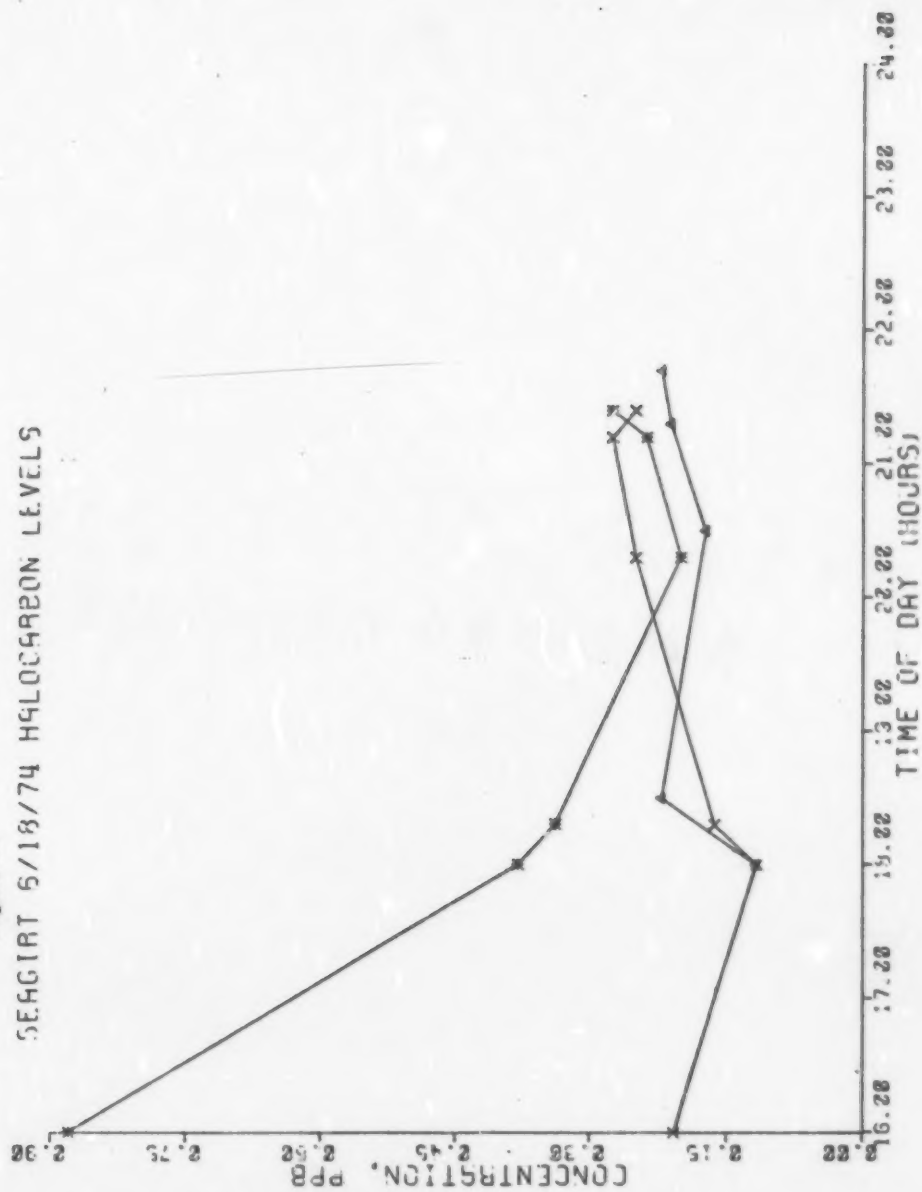
PLACE	DATE	F11	CH3I	F113	CHCl3	111T	CCl4	C2HCl3	C2Cl4	F12	SF6	O3	NOx	NO	CO	Particulates
Seagirt NJ	6/18	a	b	-	a	a	a	a	a	-	-	a	a	-	-	a
	6/19	a	a	-	a	a	a	a	a	a	-	a	a	a	-	a
N.Y. City	6/27	-	b	a	b	-	a	b	-	a	c	b	a	a	b	a
	6/28	a	b	-	b	a	a	b	-	a	-	-	a	a	b	a
Sandy Hook NJ	7/2	a	a	a	b	a	a	a	a	-	-	a	a	b	-	a
	7/3	a	a	a	b	a	a	a	a	a	a	a	a	b	b	a
	7/4	a	a	a	b	a	a	a	a	a	b	a	a	b	b	a
	7/5	a	a	a	b	a	a	-	a	-	b	a	a	b	-	a
Wilm. Del.	7/8	a	b	-	-	a	a	a	a	a	a	b	a	a	b	a
	7/9	a	b	-	-	a	a	a	a	a	-	a	a	a	-	a
	7/10	a	b	-	-	a	a	-	a	a	a	-	a	a	-	a
Balt. Md.	7/11	a	b	a	-	a	a	-	a	a	a	b	a	a	b	a
	7/12	a	b	-	-	a	a	-	a	a	b	a	a	a	b	a
Wilm. Ohio	7/19	-	-	-	-	-	-	-	-	-	-	-	a	a	b	a
	7/21	a	-	b	-	a	a	-	-	a	-	a	a	-	b	a
	7/22	a	-	b	a	a	a	-	a	a	-	-	a	-	b	a
	7/23	a	-	b	a	a	a	a	a	a	-	-	a	-	b	a
	7/24	a	-	b	a	a	a	a	a	a	-	-	a	-	b	a
	7/25	a	-	b	a	a	a	-	-	-	-	-	a	-	b	a
	7/26	-	-	-	-	-	-	-	-	-	-	-	a	-	b	a
	7/27	-	-	-	-	-	-	-	-	-	-	-	a	-	-	a
White-face Mt. NY	9/16	a	b	-	b	a	a	a	a	a	a	-	a	a	-	a
	9/17	a	-	-	b	a	a	a	a	a	a	-	a	a	-	a
	9/18	a	-	-	b	a	a	-	a	a	-	-	a	a	-	a
	9/19	a	-	-	-	a	a	-	a	-	-	-	a	a	-	a

a = scale factor of 10-3
b = scale factor of 10-2
c = scale factor of 10-1

TABLE 19B. Key to Symbols used in Figures 31-77

Z	- O ₃
Y	- CO
I	- PART.
☆	- NO
⊗	- NO _x
⊠	- SF ₆
⊙	- F-12
✱	- C ₂ Cl ₄
⊕	- C ₂ HCl ₃
△	- CCl ₄
◊	- 111T
+	- CHCl ₃
⊗	- F113
□	- CH ₃ l
×	- F-11

Figure 31
SERGIAT 6/18/74 HYDROCARBON LEVELS



SEAGIAT 6/18/74 HALOCARBON LEVELS

Figure 31A

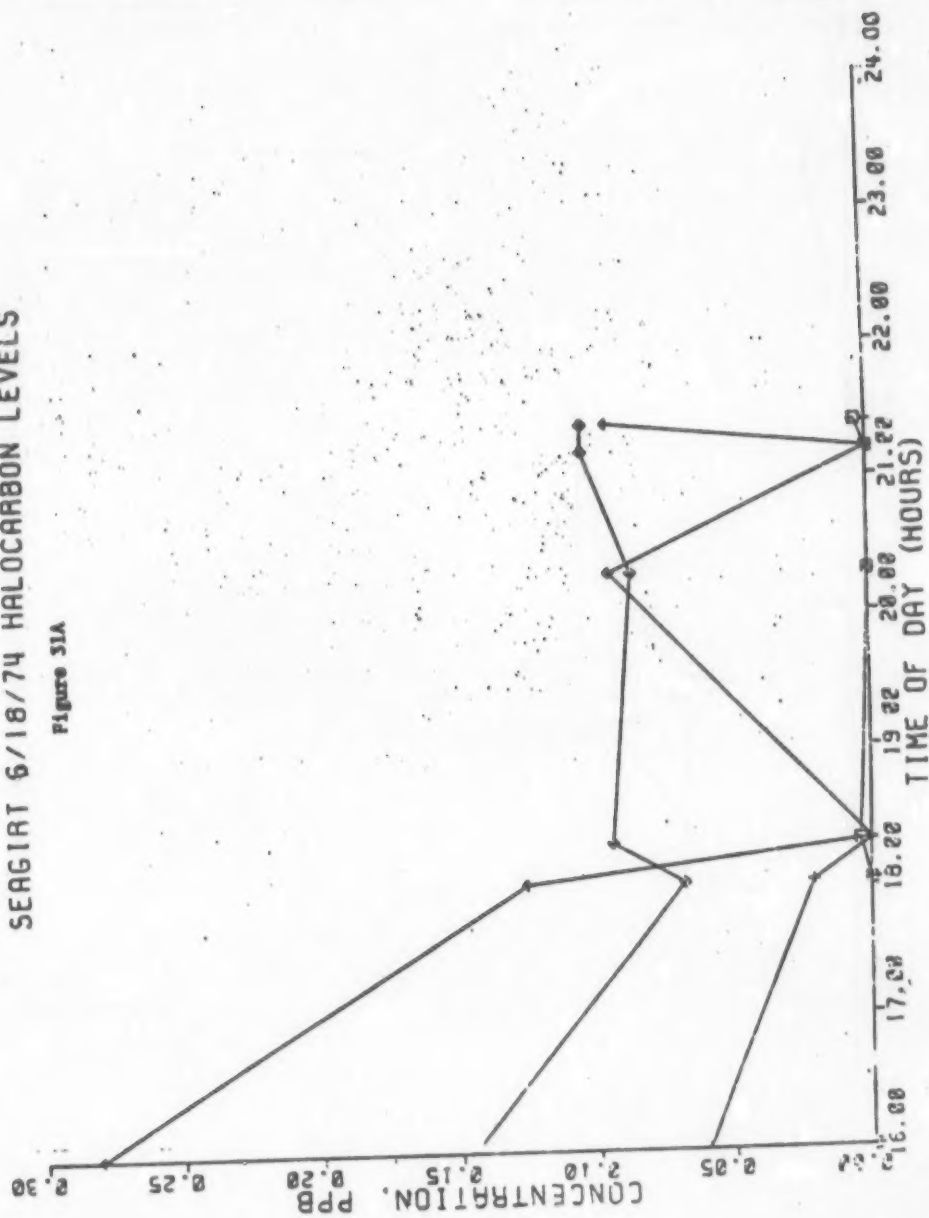
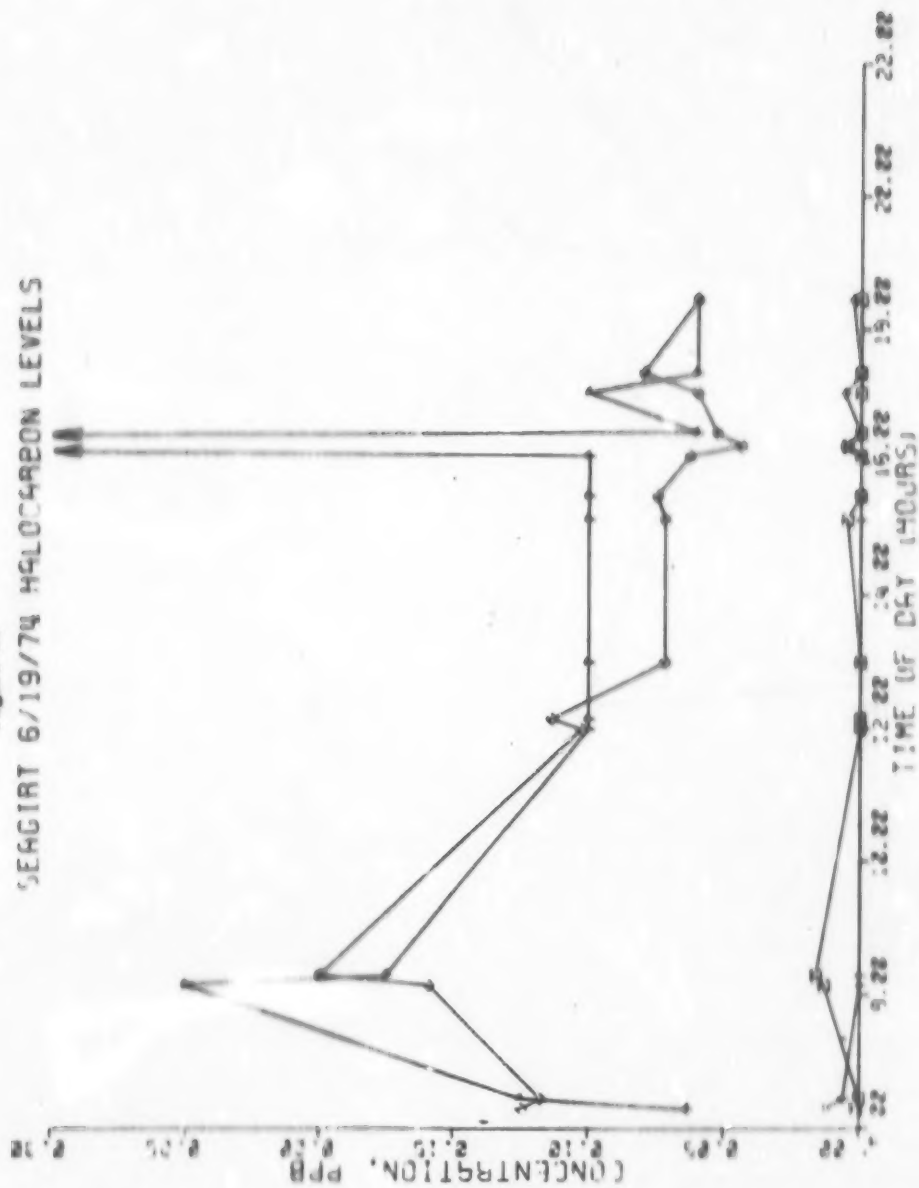
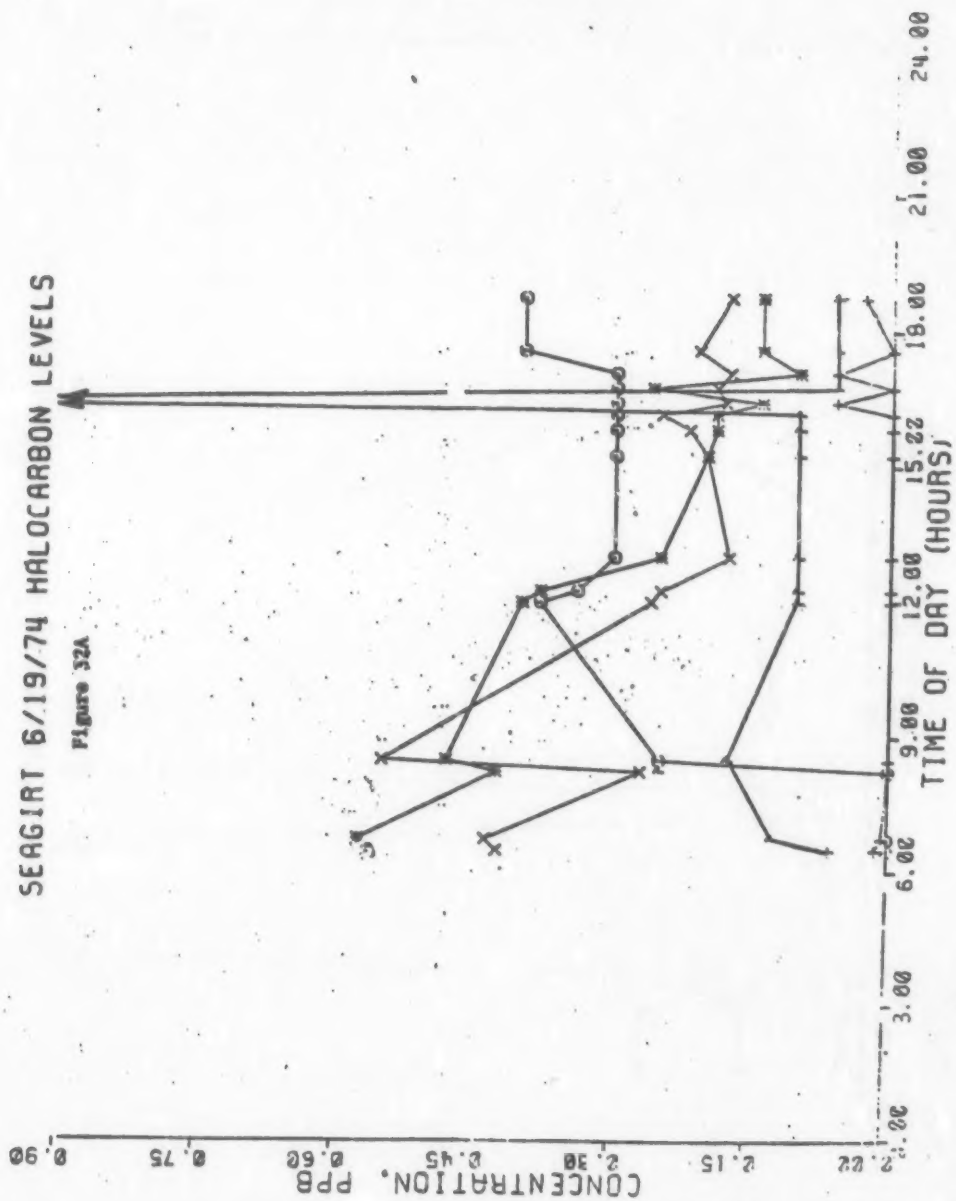
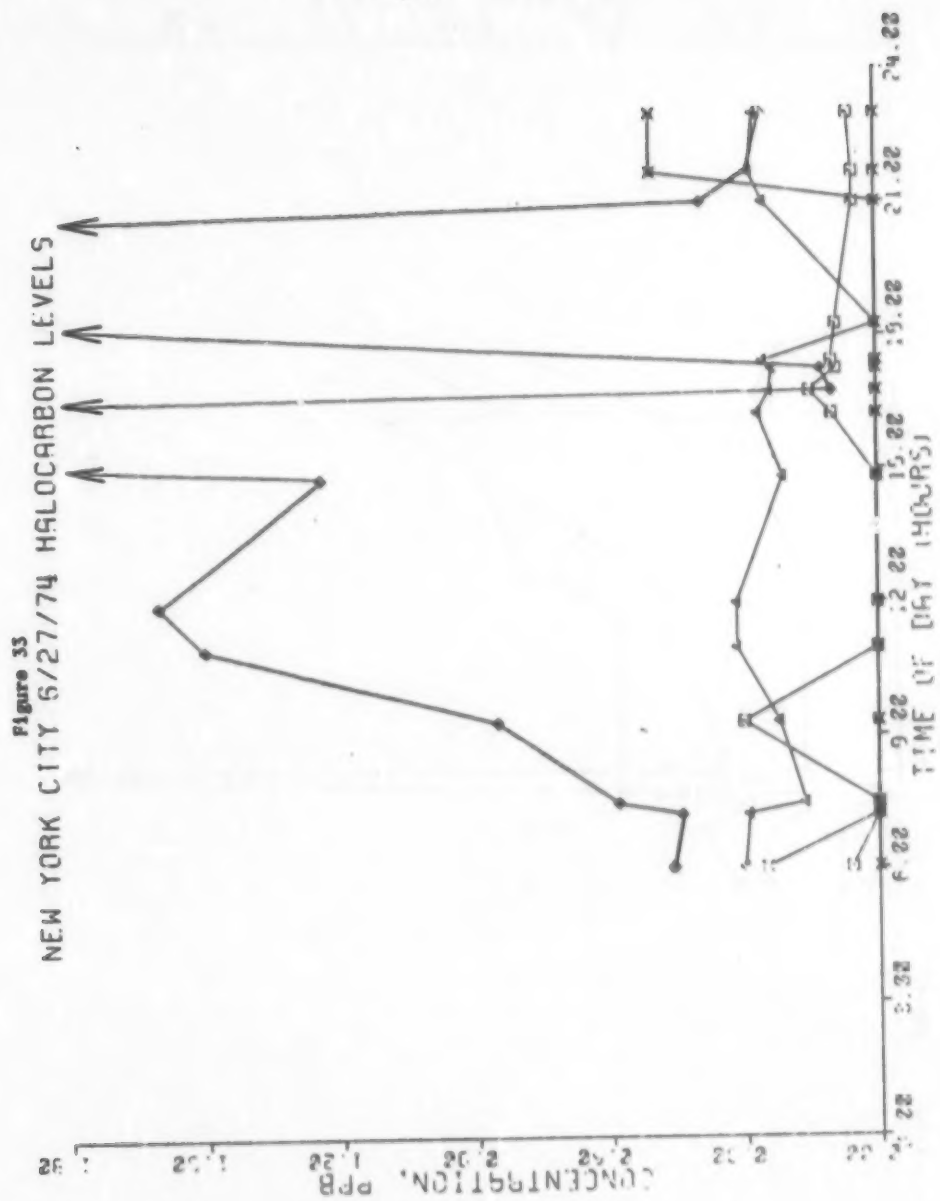


Figure 32
SERGIAT 6/19/74 HALOCARBON LEVELS







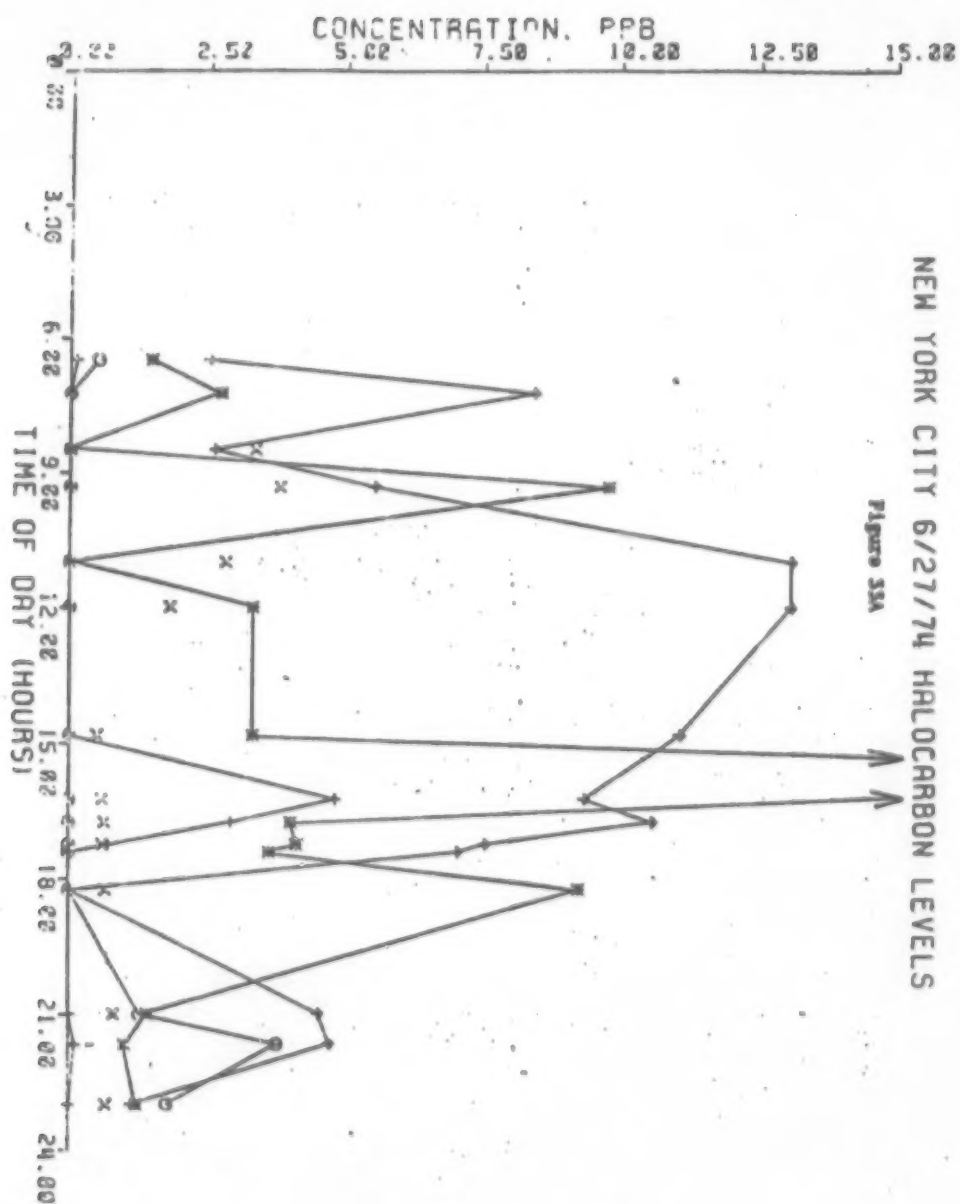
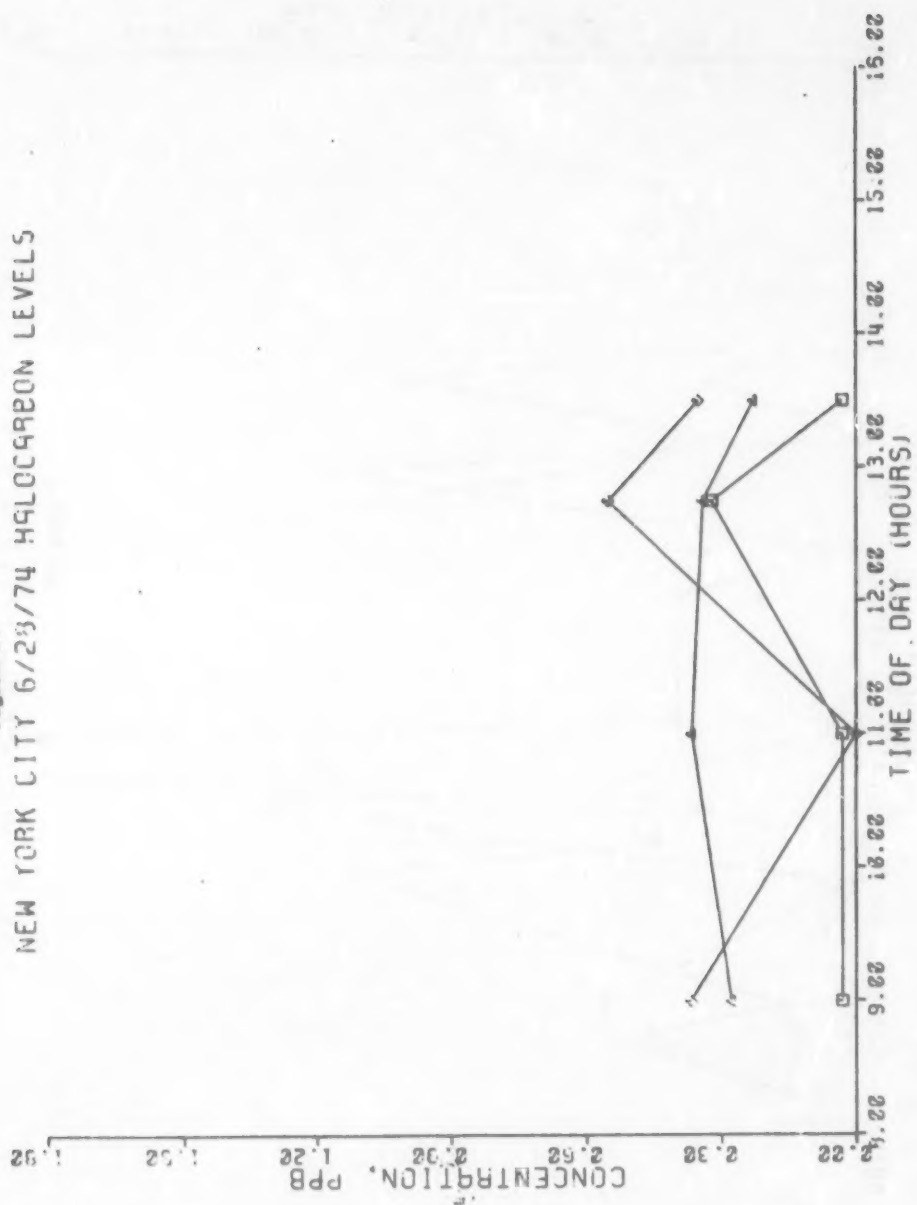


Figure 34
NEW YORK CITY 6/23/74 HALOCARBON LEVELS



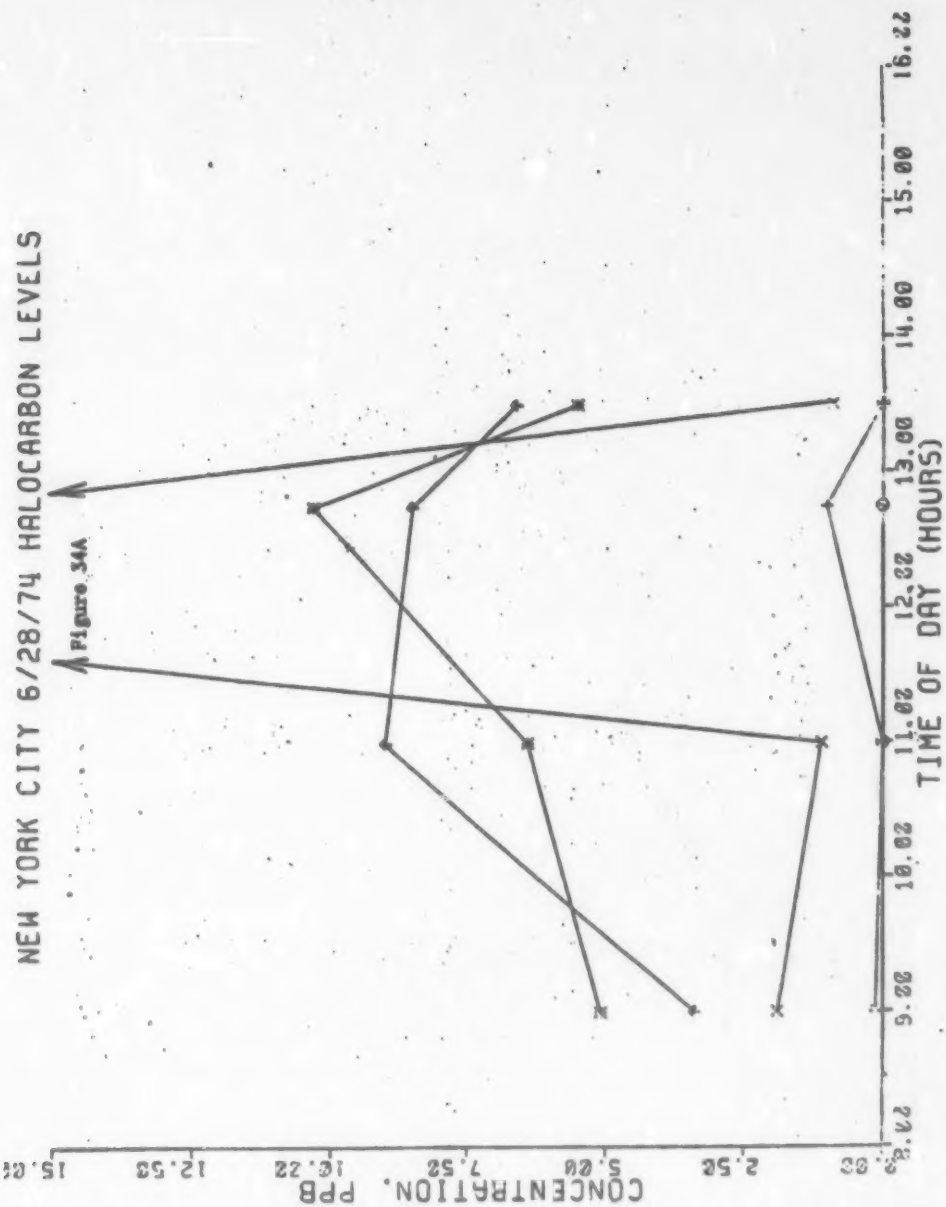
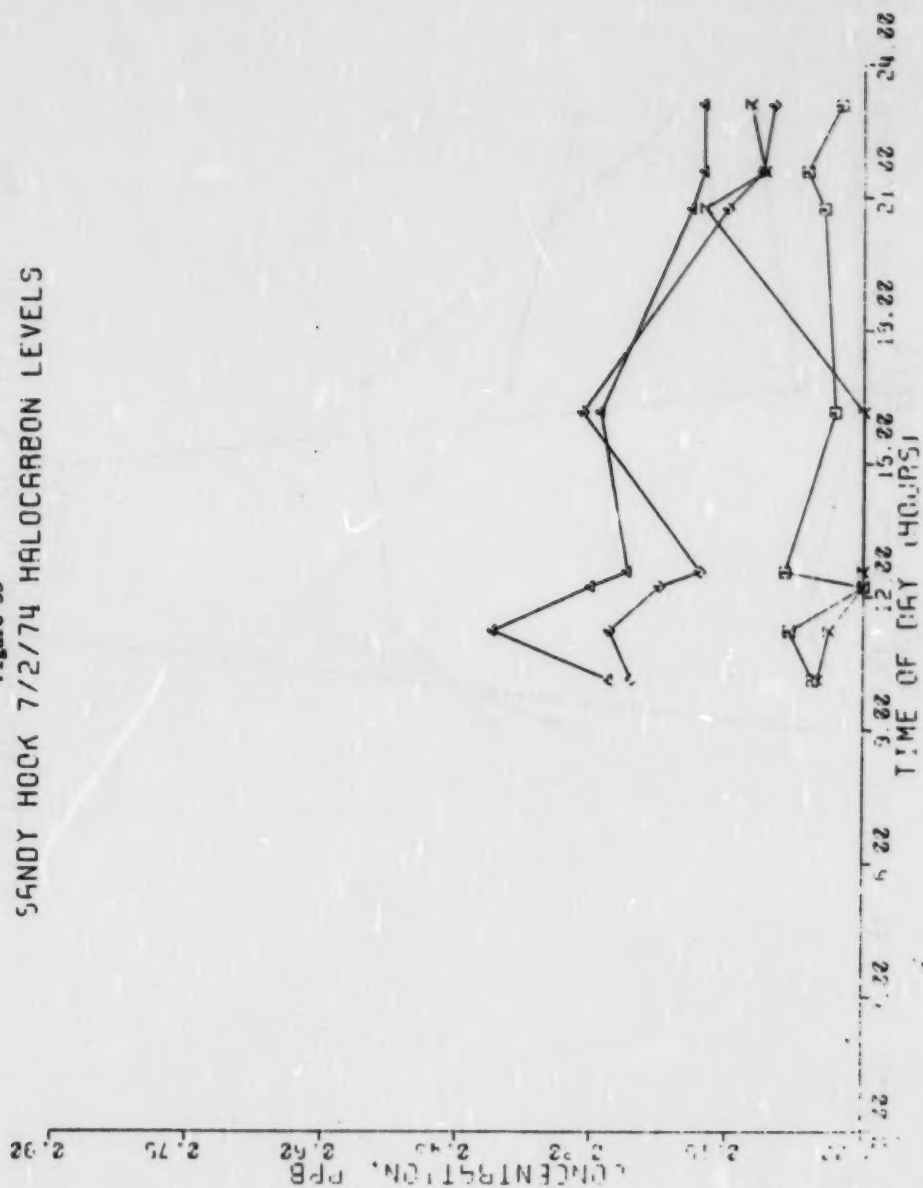
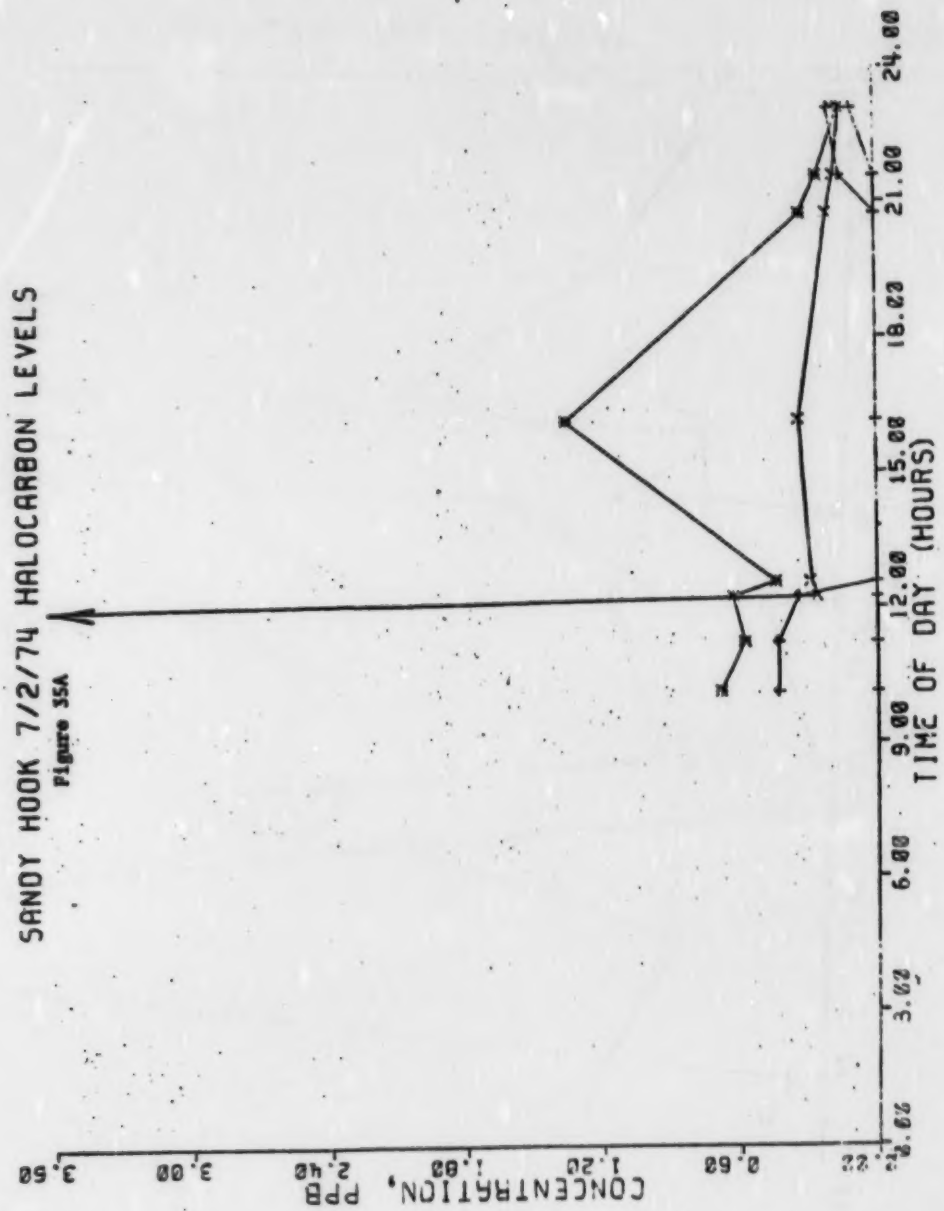
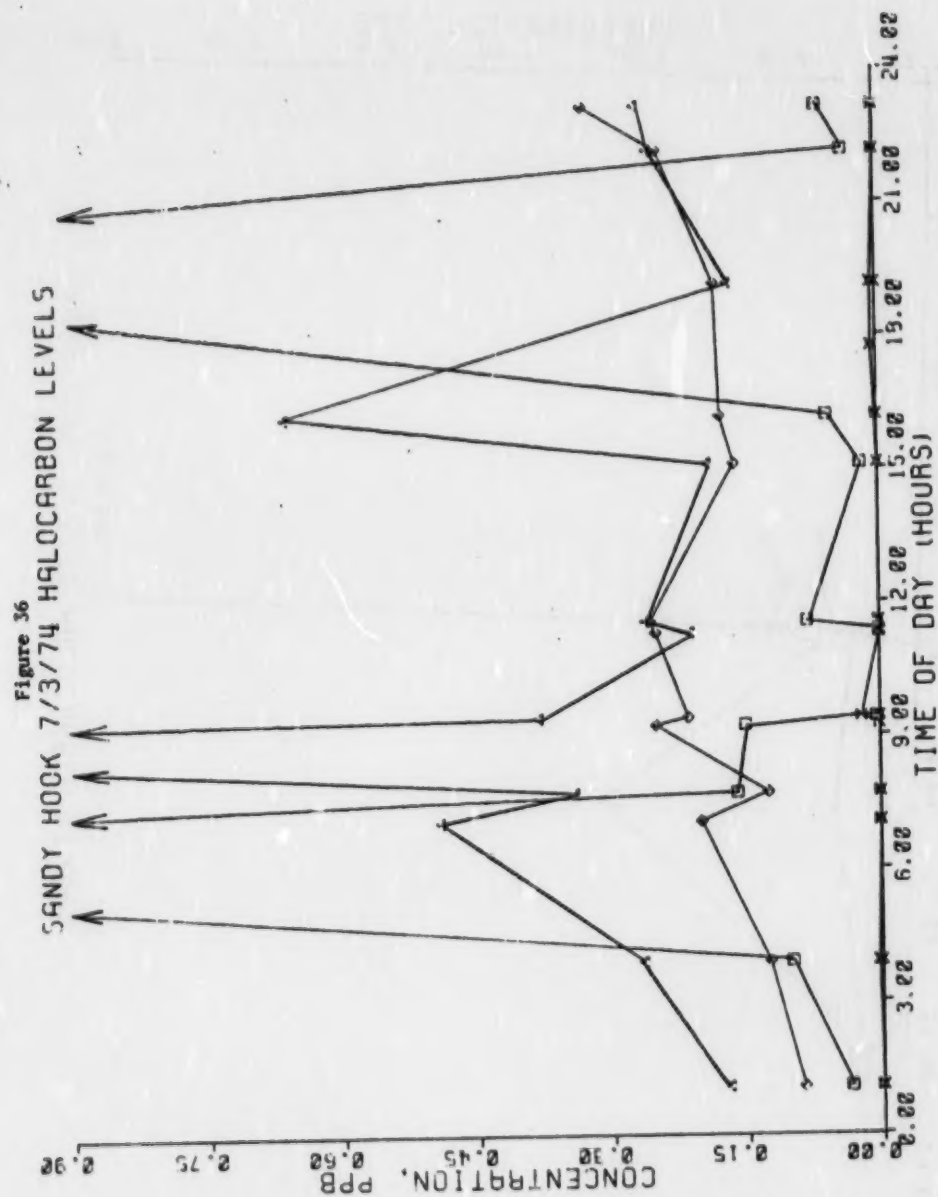
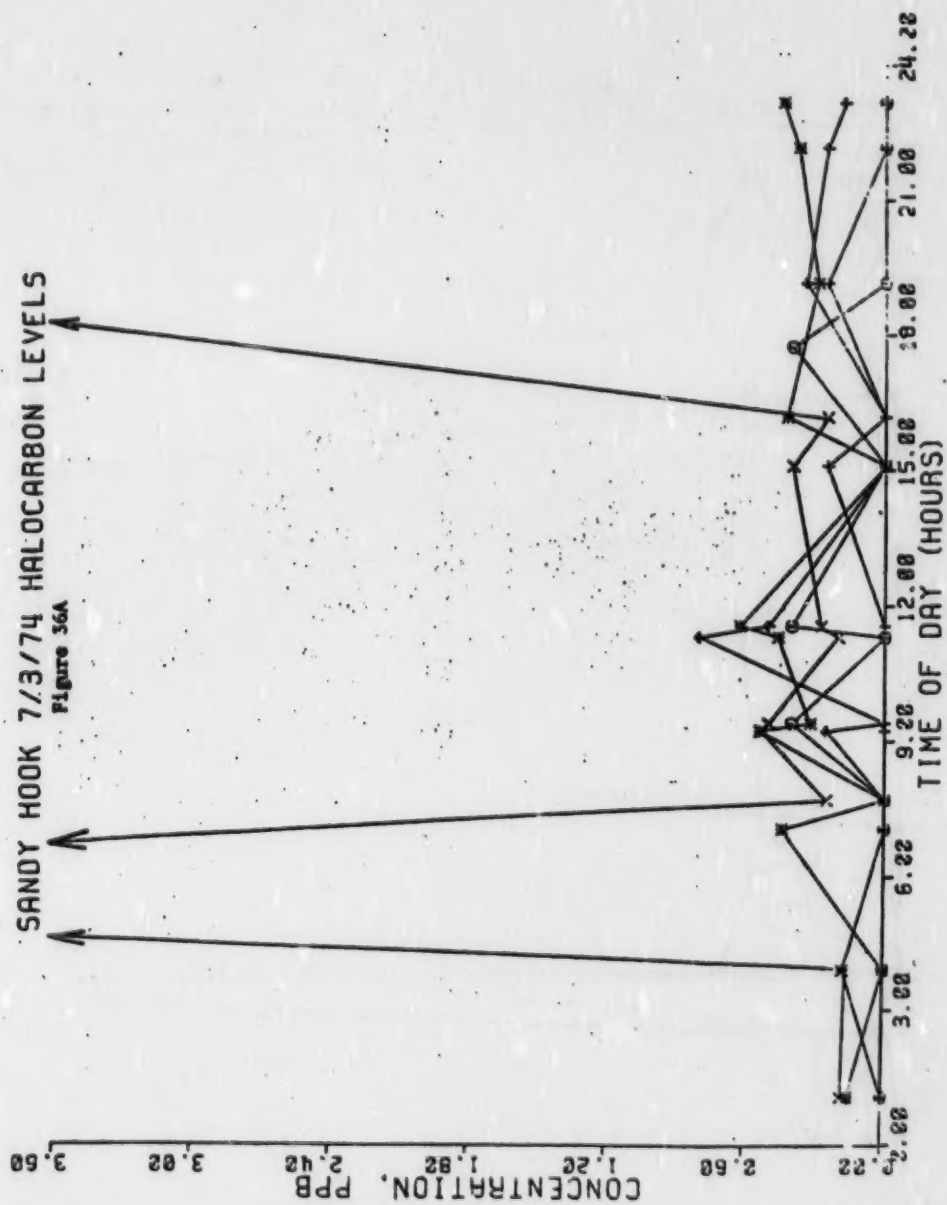


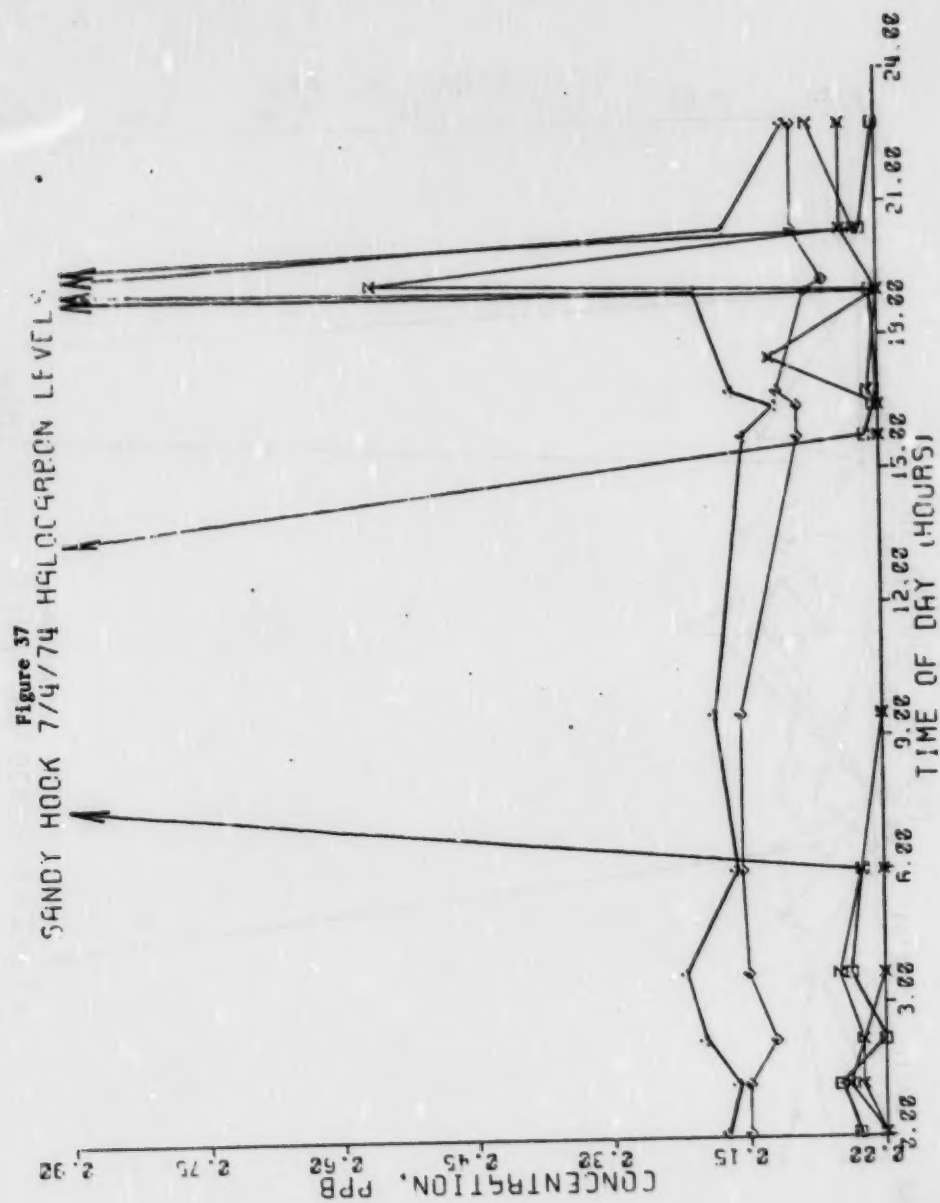
Figure 35
SANDY HOOK 7/2/74 HALOCARBON LEVELS











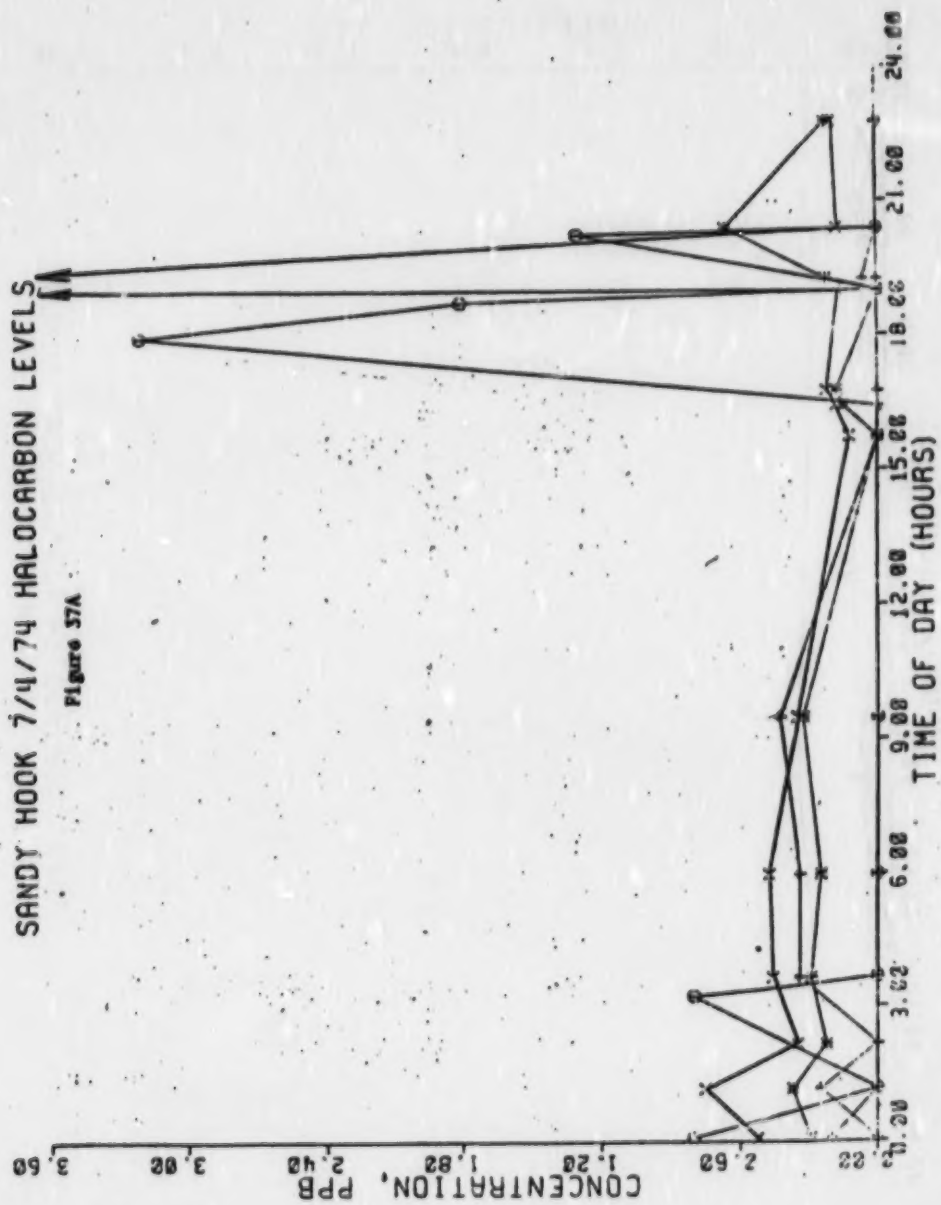
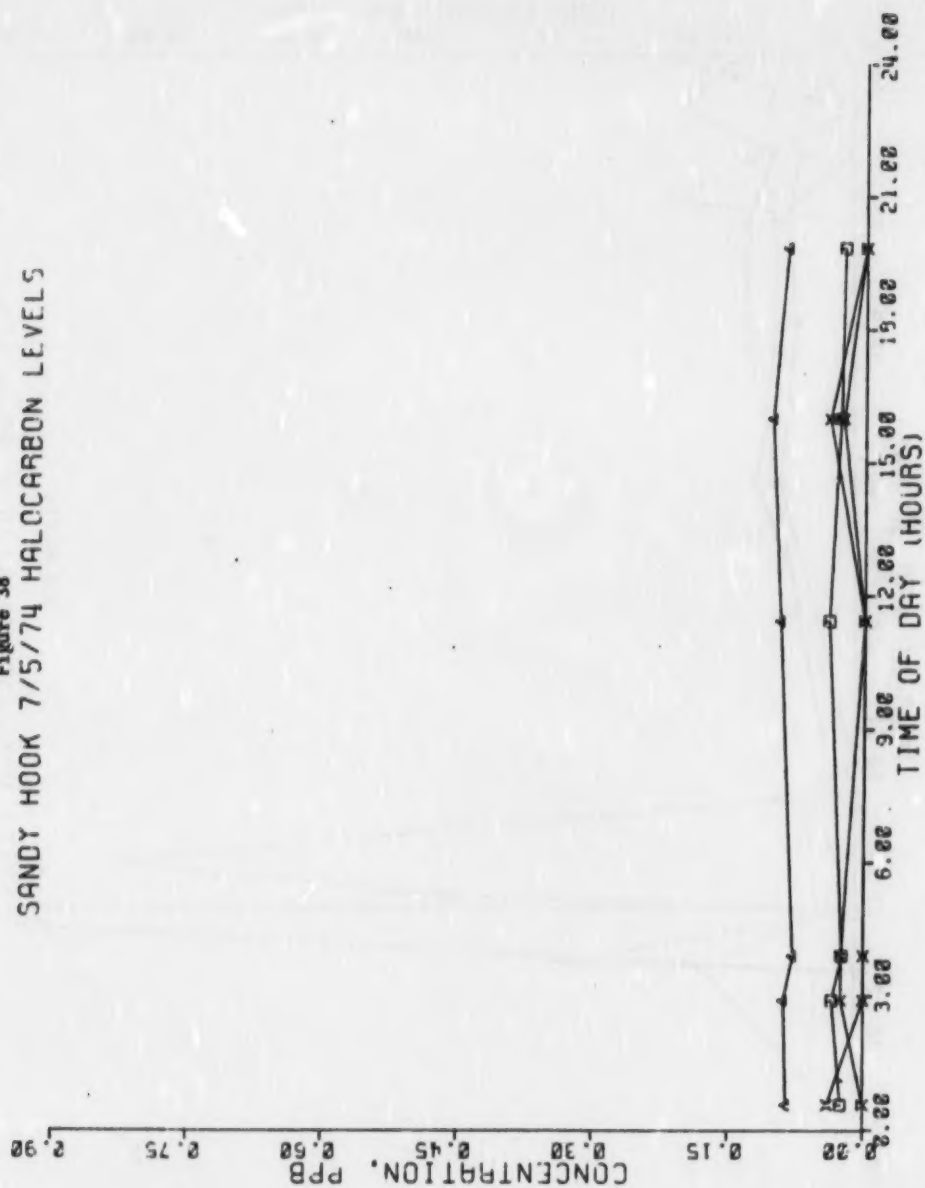
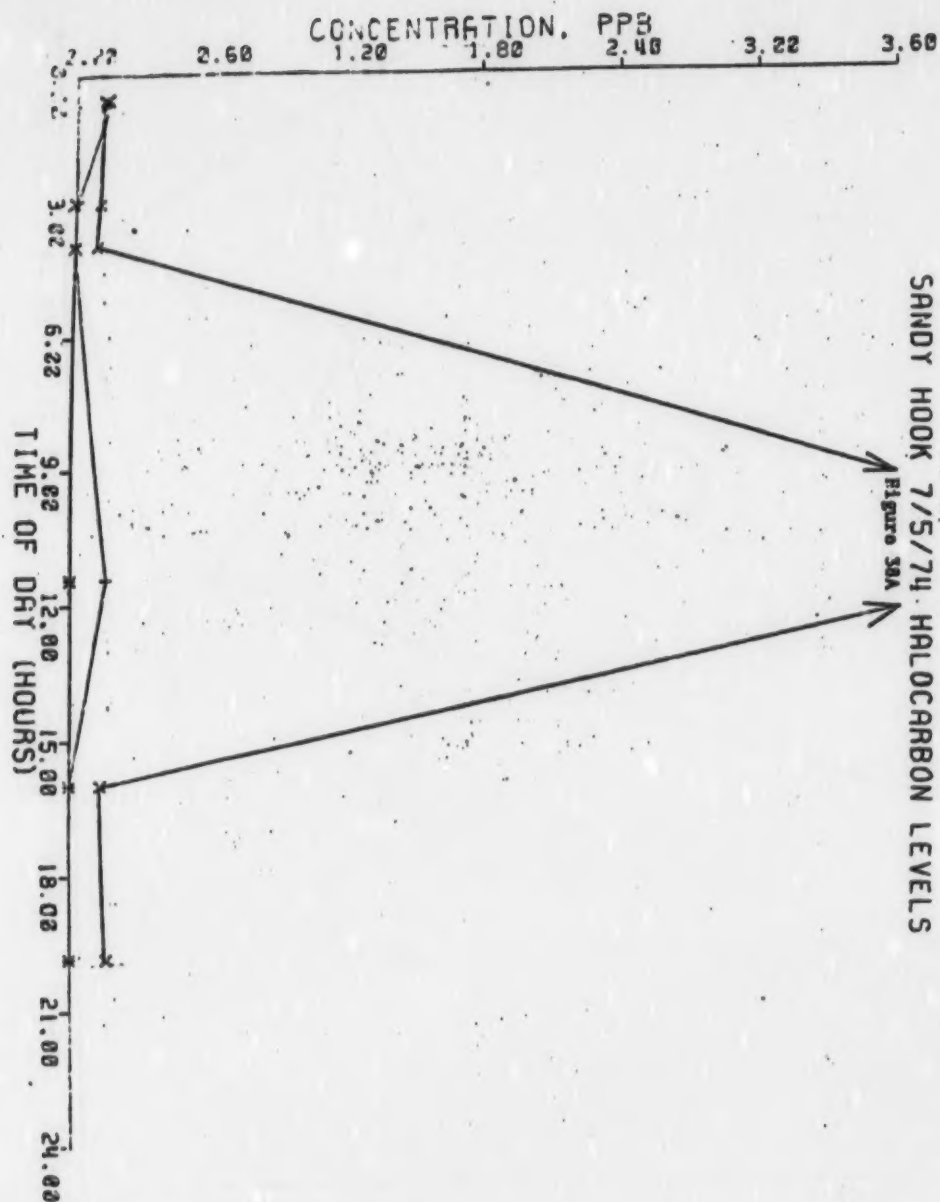
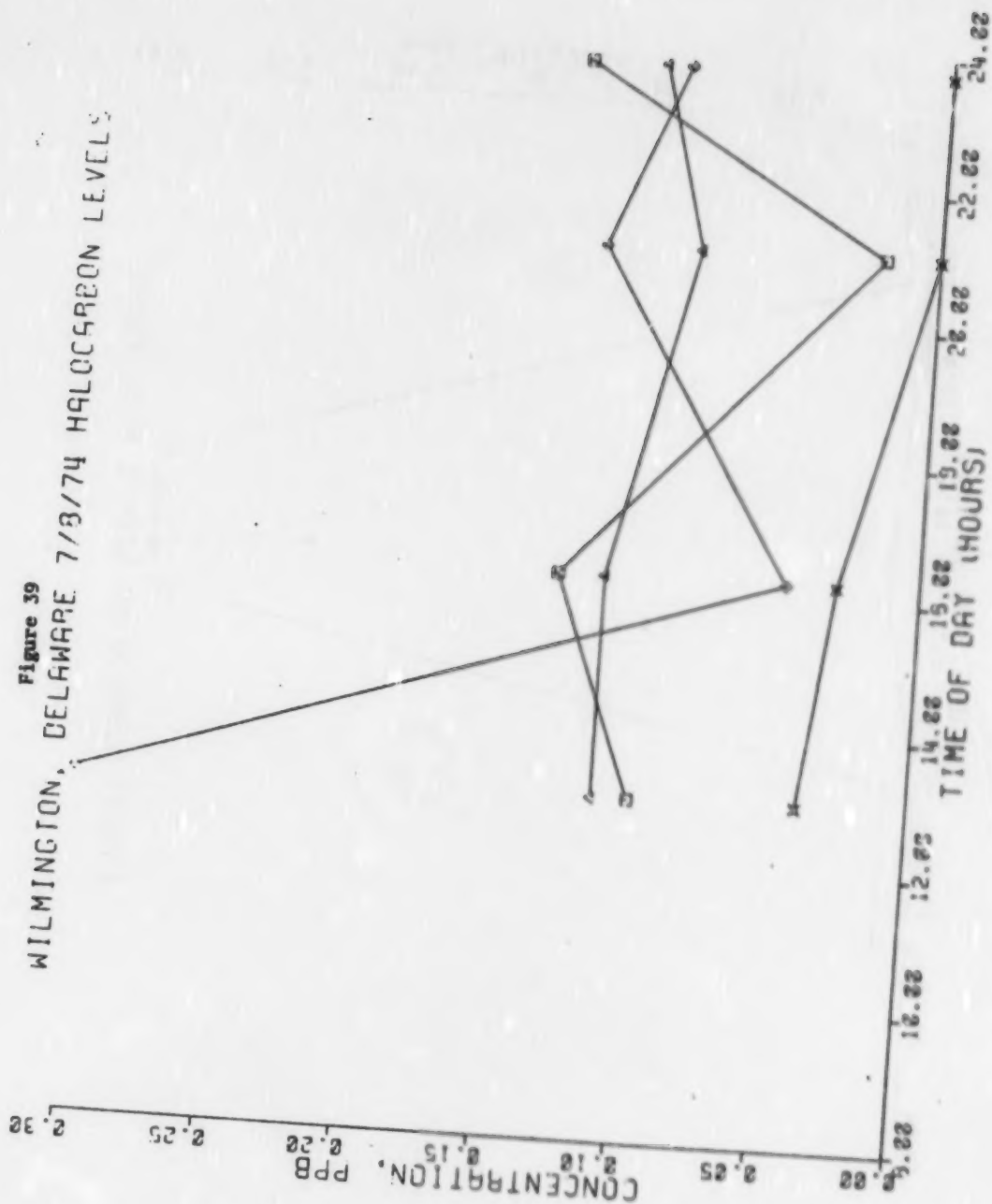


Figure 38
SANDY HOOK 7/5/74 HALOCARBON LEVELS

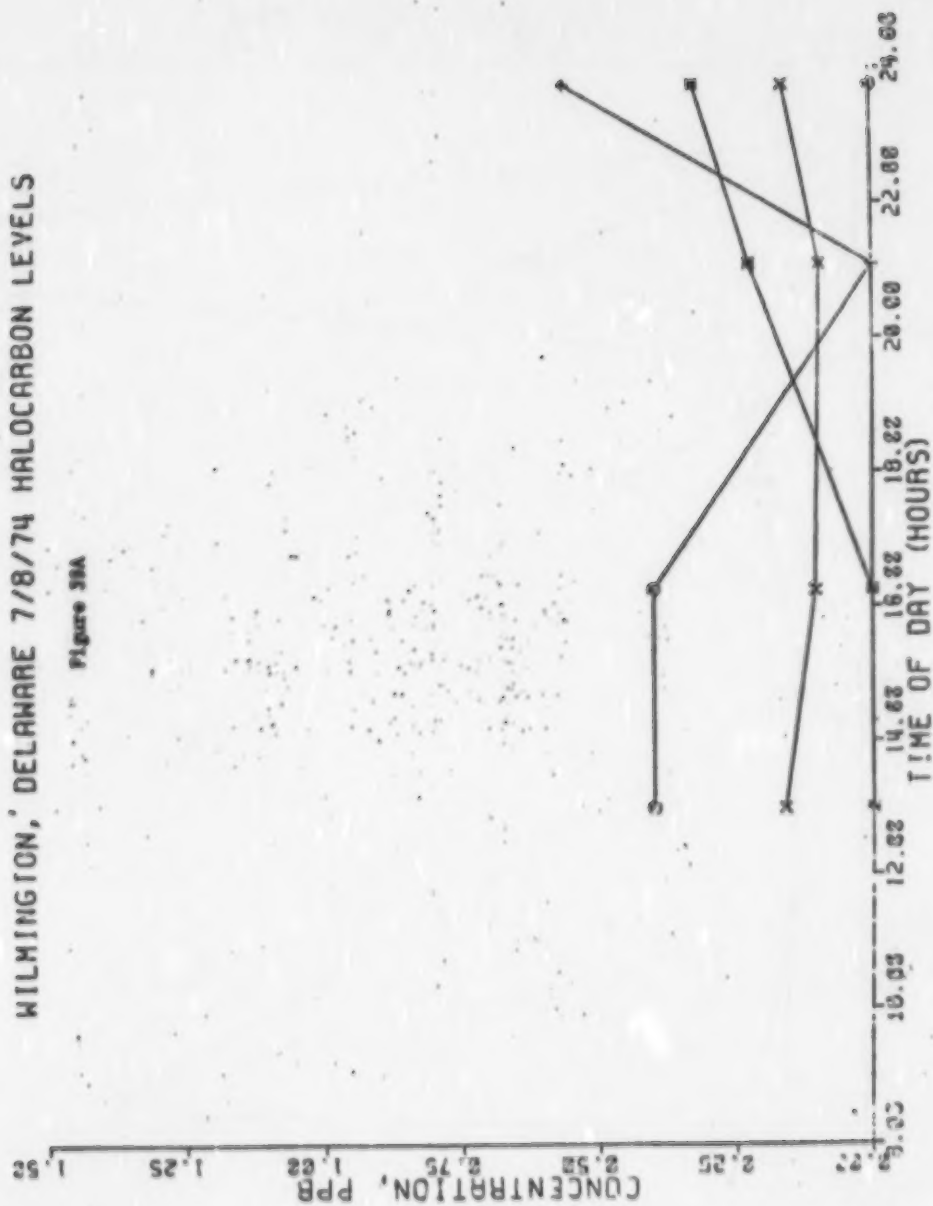


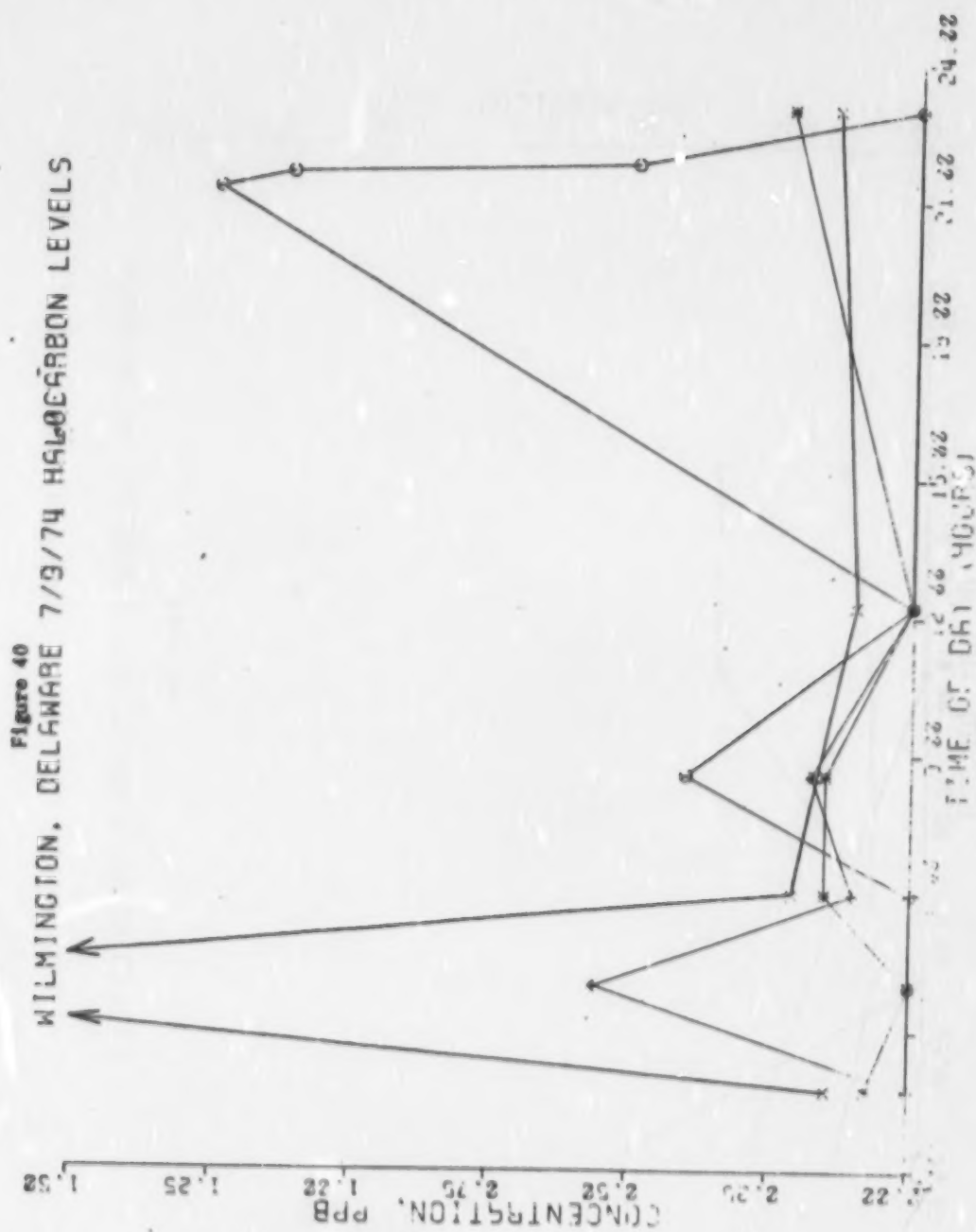




WILMINGTON, DELAWARE 7/8/74 HALOCARBON LEVELS

Figure 39A





WILMINGTON, DELAWARE 7/9/74 HALOCARBON LEVELS

Figure 40A

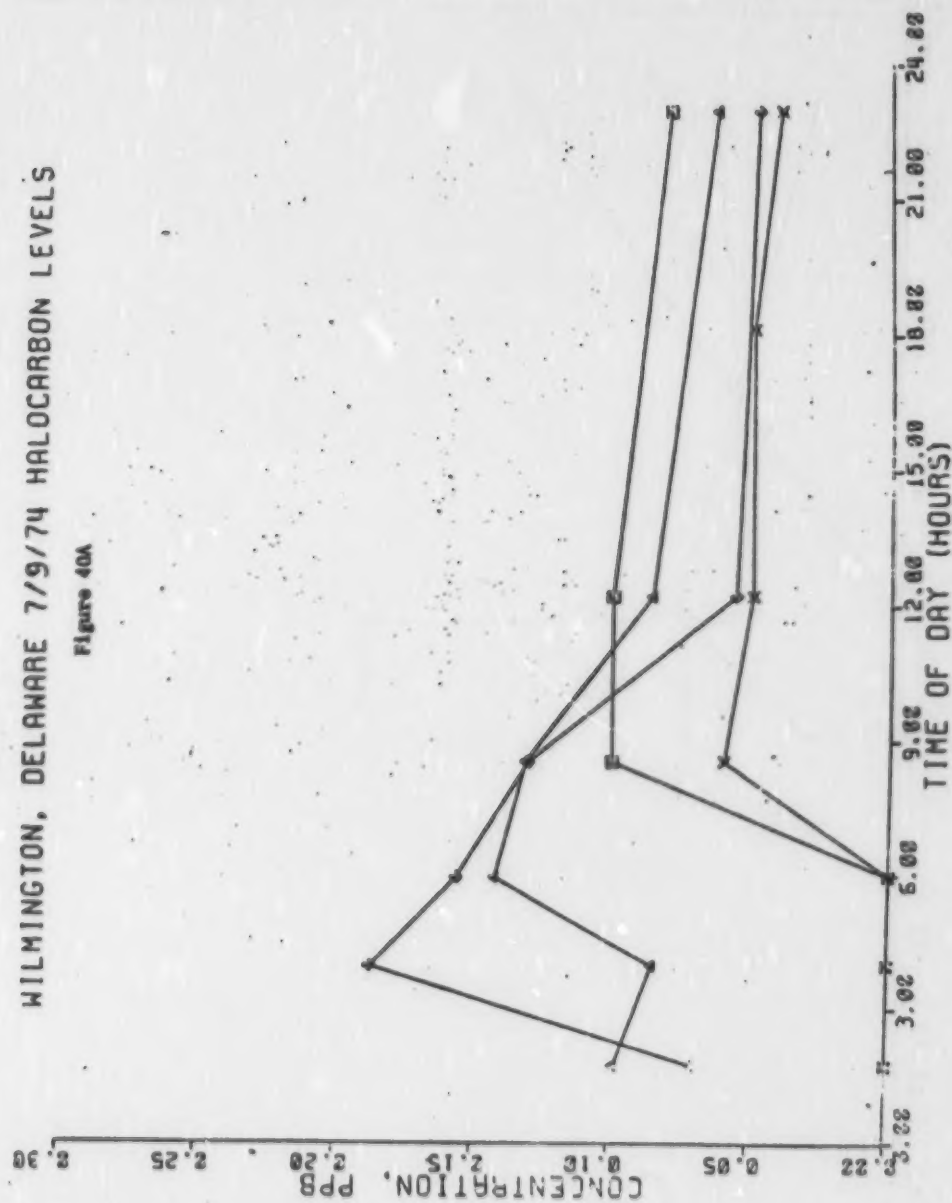
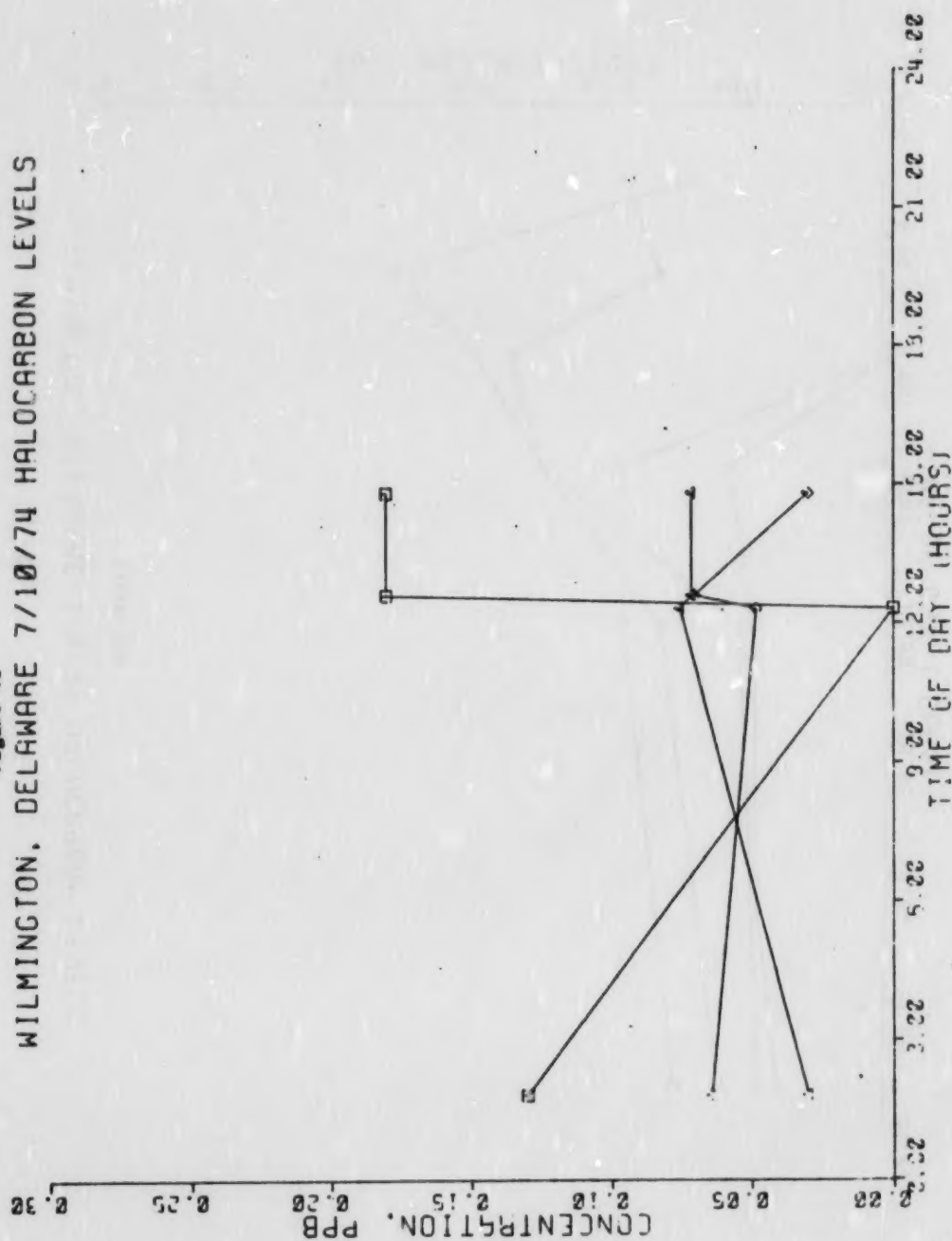


Figure 41
WILMINGTON, DELAWARE 7/10/74 HALOCARBON LEVELS



WILMINGTON, DELAWARE 7/10/74 HALOCARBON LEVELS

Figure 41A

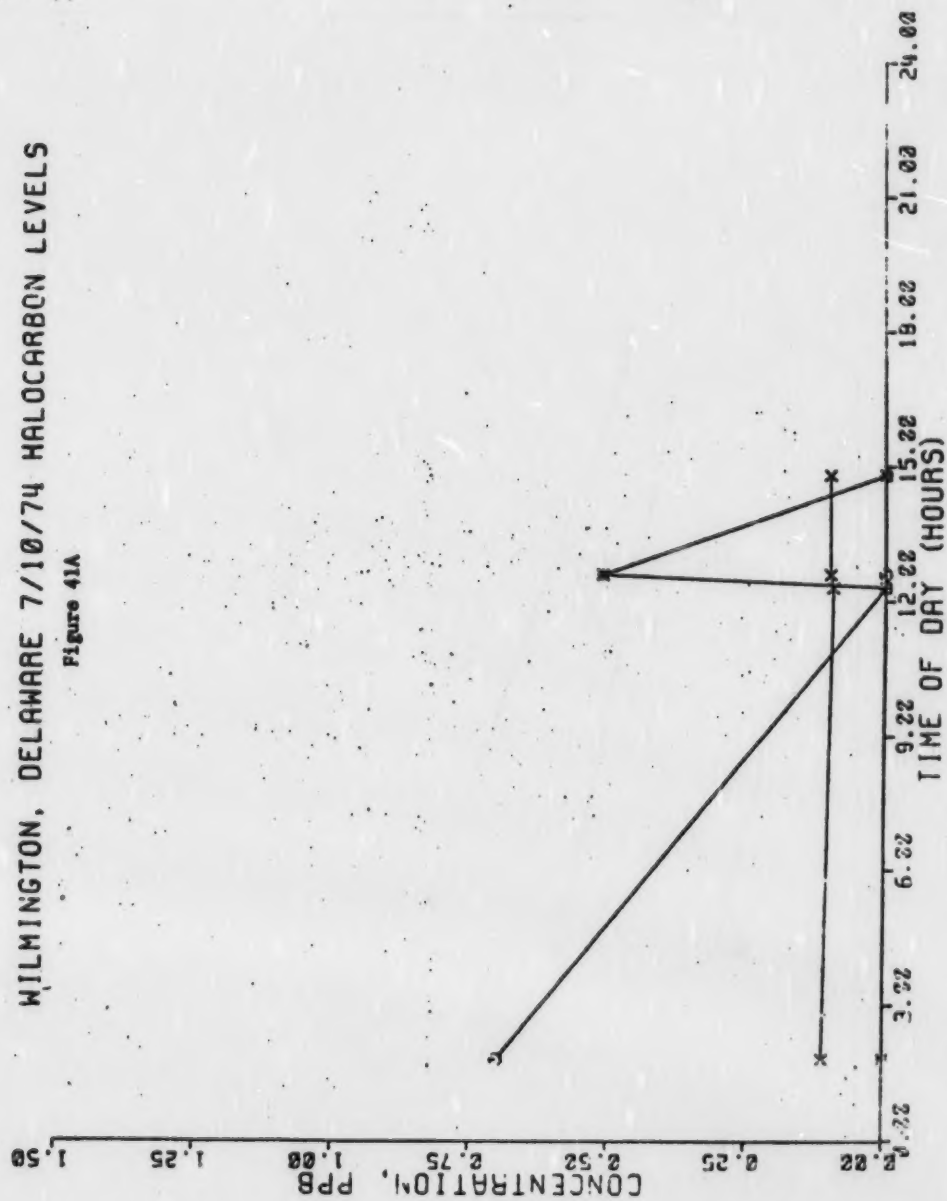
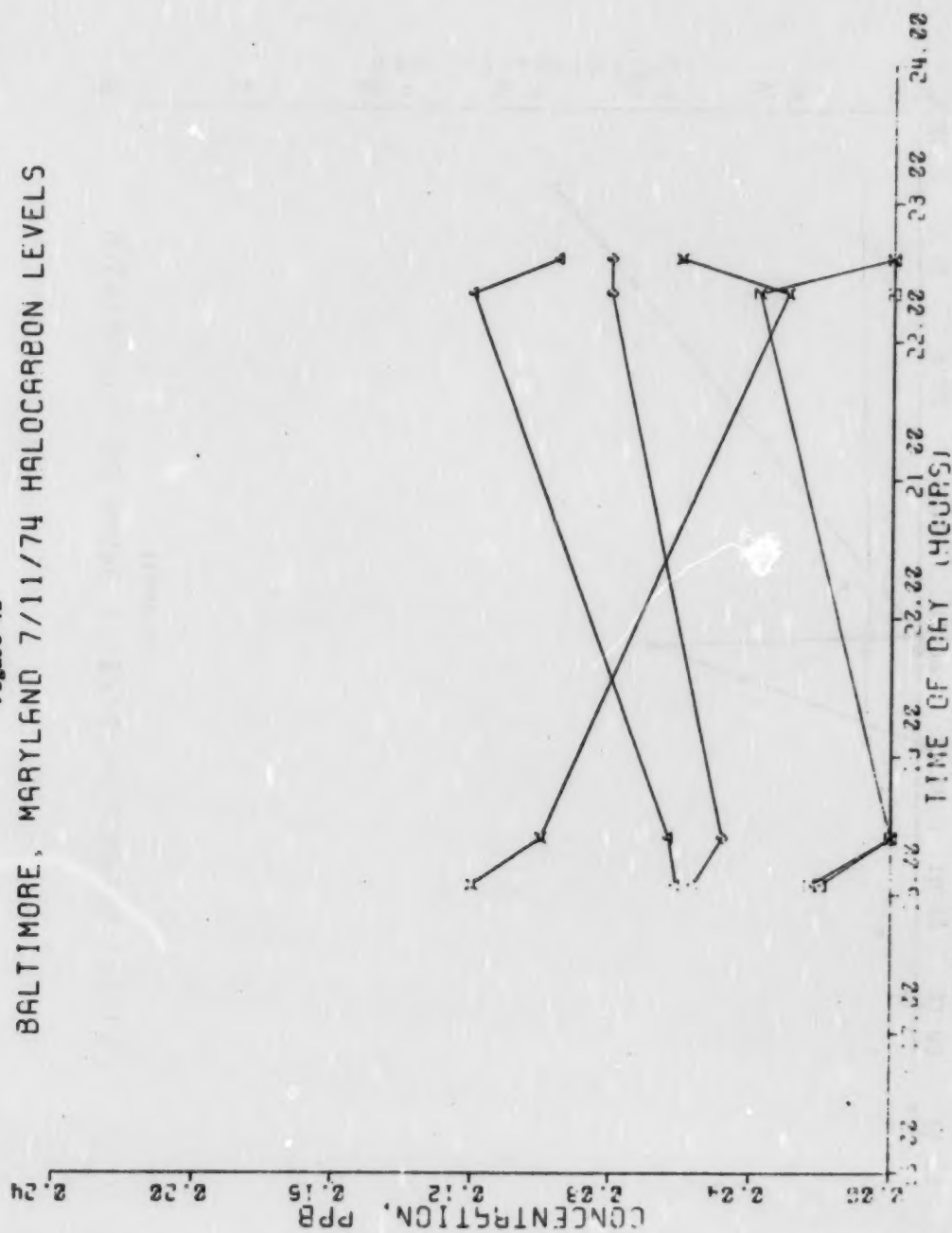


Figure 42
BALTIMORE, MARYLAND 7/11/74 HALOCARBON LEVELS



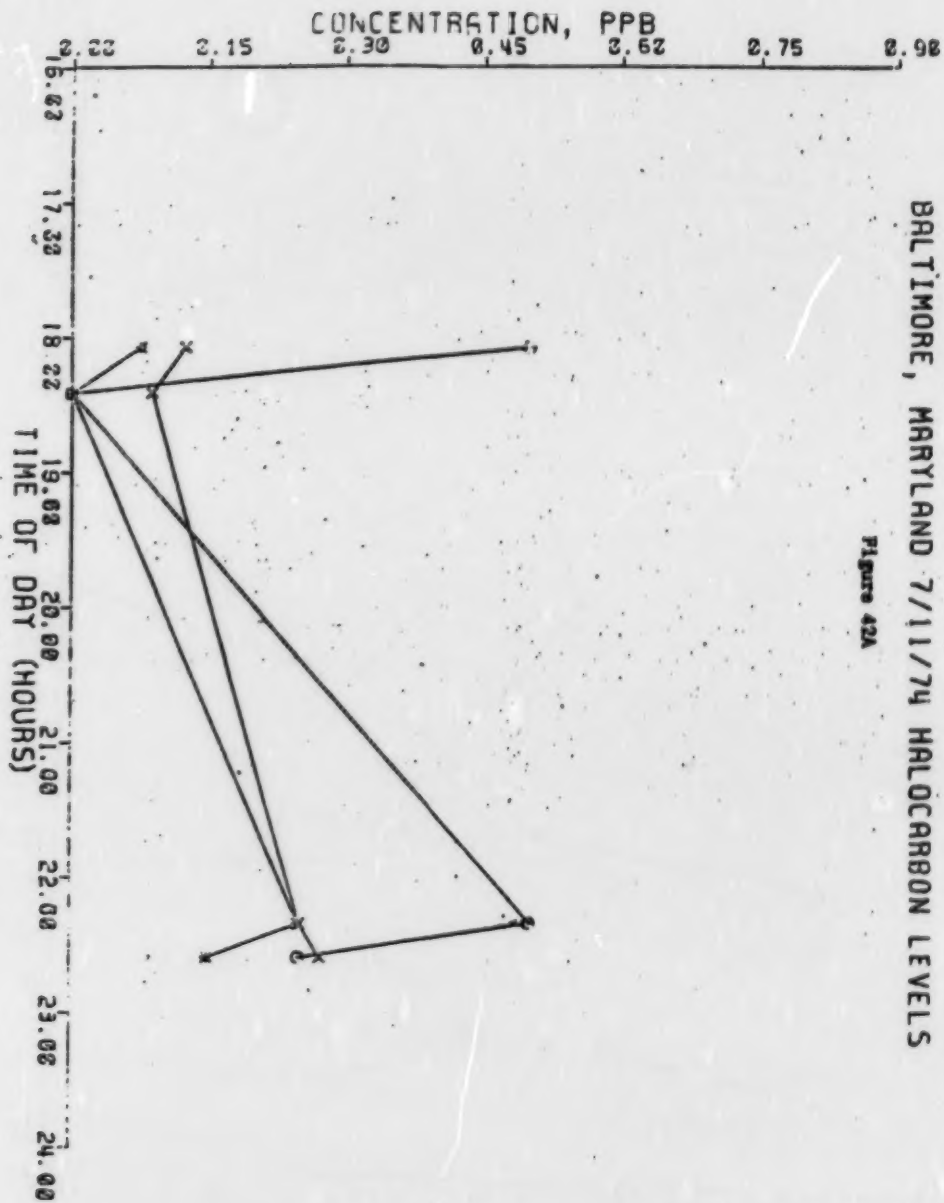
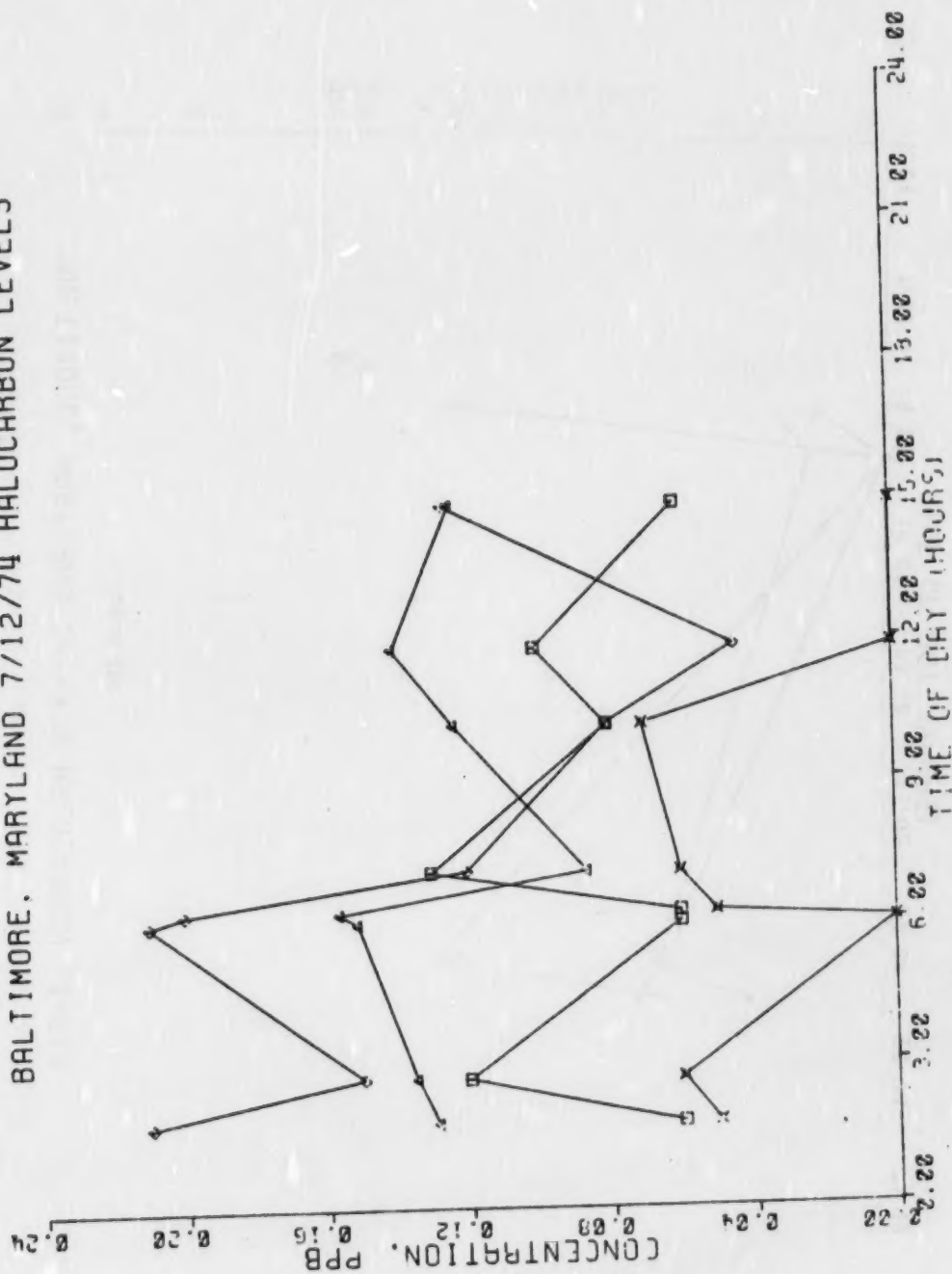


Figure 43
BALTIMORE, MARYLAND 7/12/74 HALOCARBON LEVELS



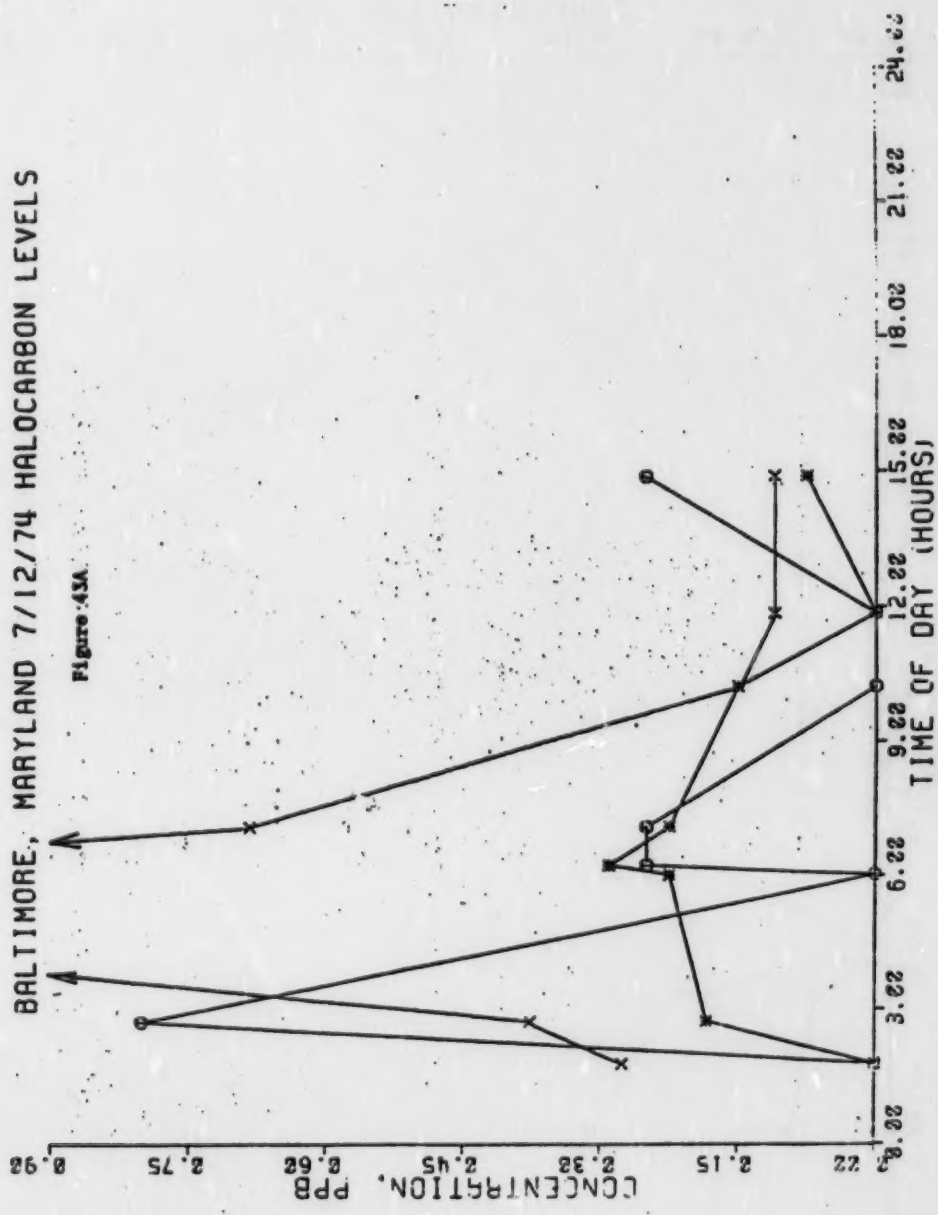
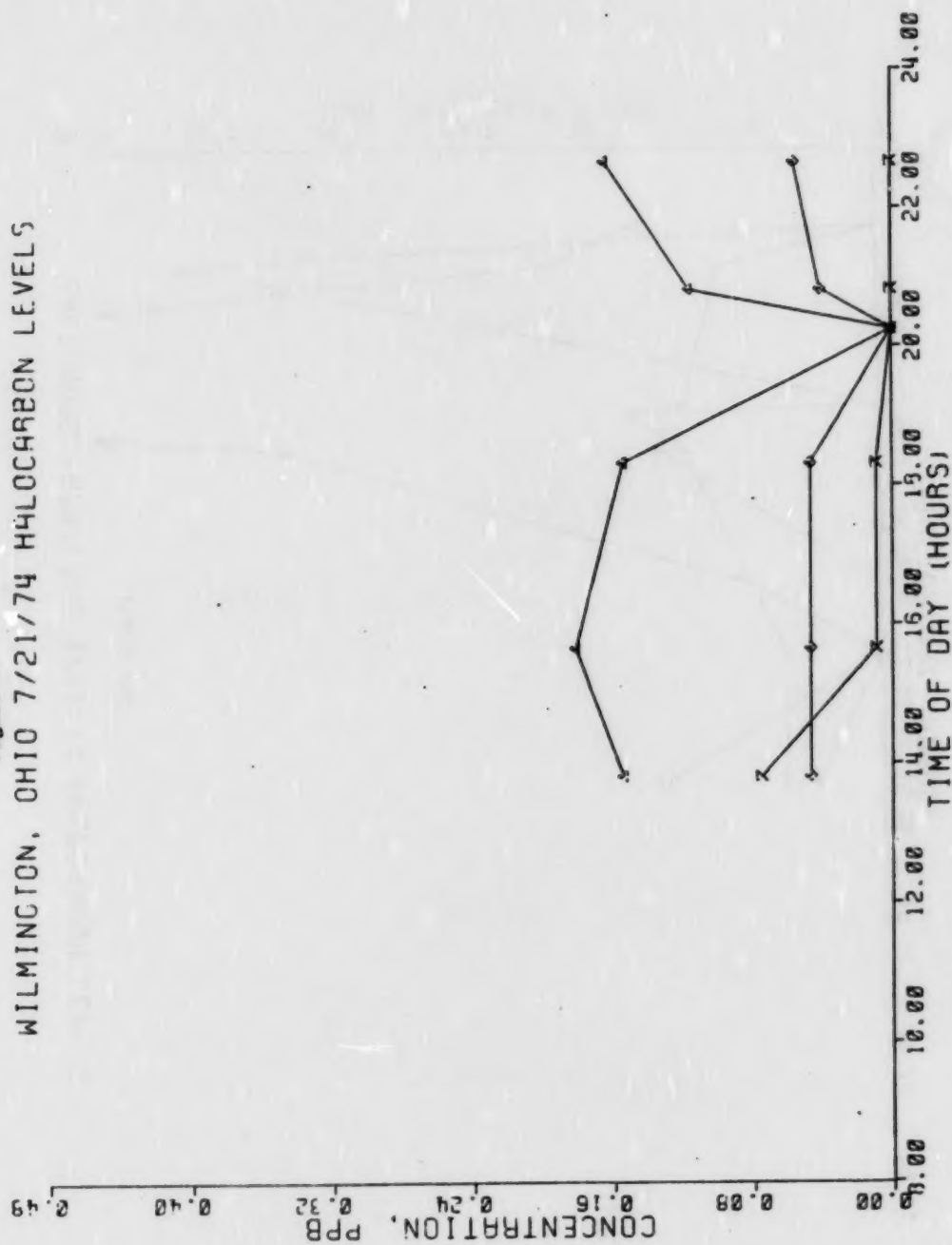
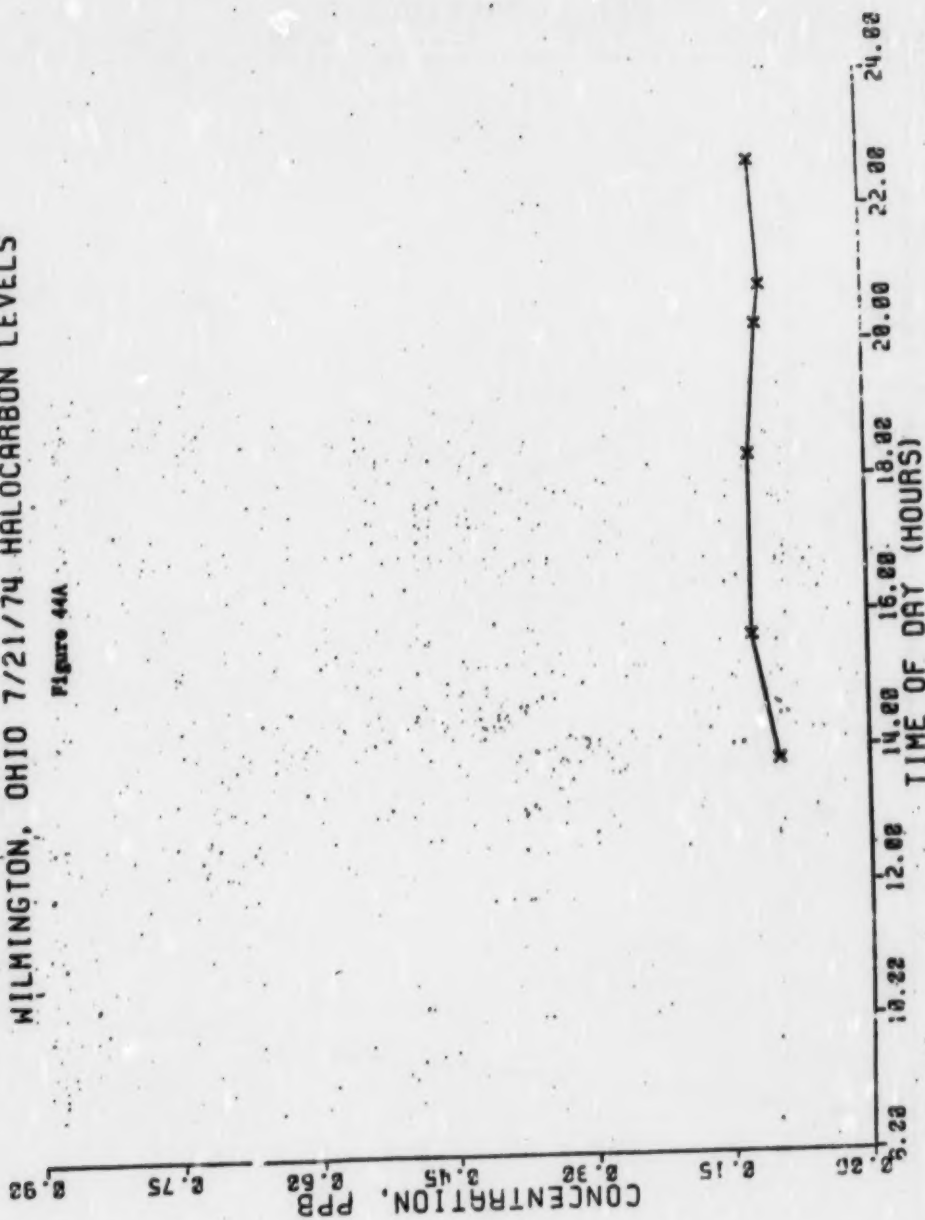


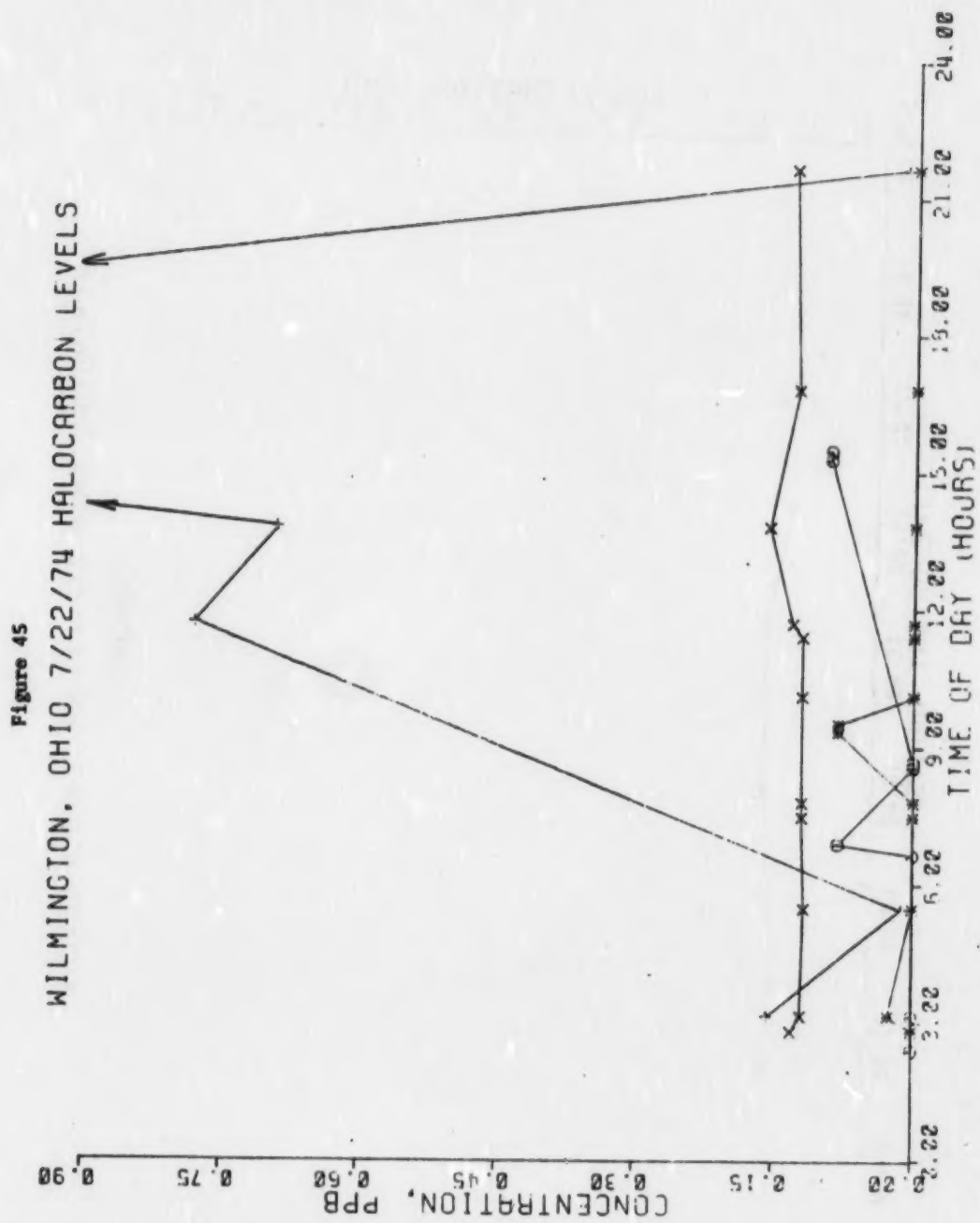
Figure 44
WILMINGTON, OHIO 7/21/74 H4LOCARBON LEVELS



WILMINGTON, OHIO 7/21/74 HALOCARBON LEVELS

Figure 44A





WILMINGTON, OHIO 7/22/74 HALOCARBON LEVELS

Figure 45A

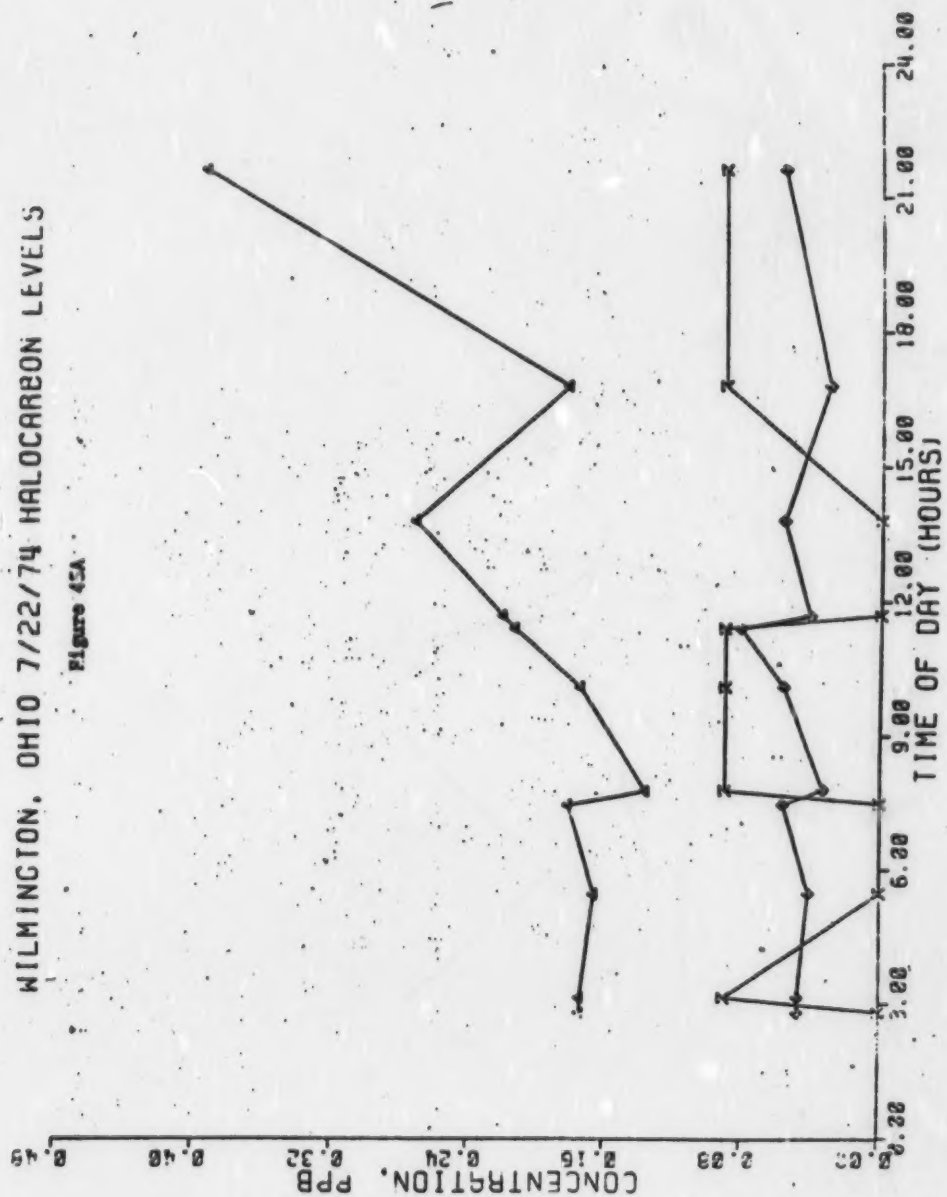
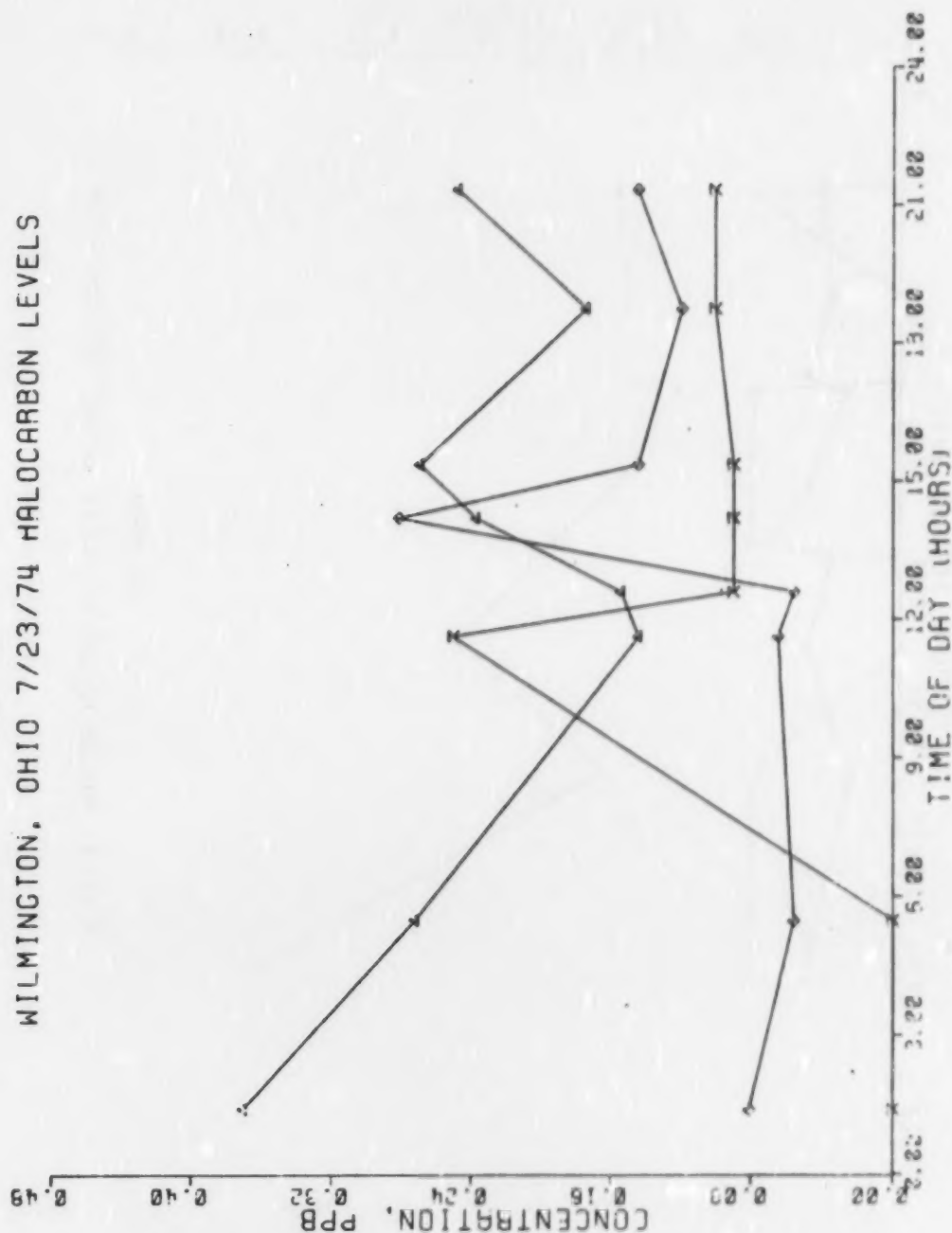


Figure 46
WILMINGTON, OHIO 7/23/74 HALOCARBON LEVELS



WILMINGTON, OHIO 7/23/74 HALOCARBON LEVELS

Figure 46A

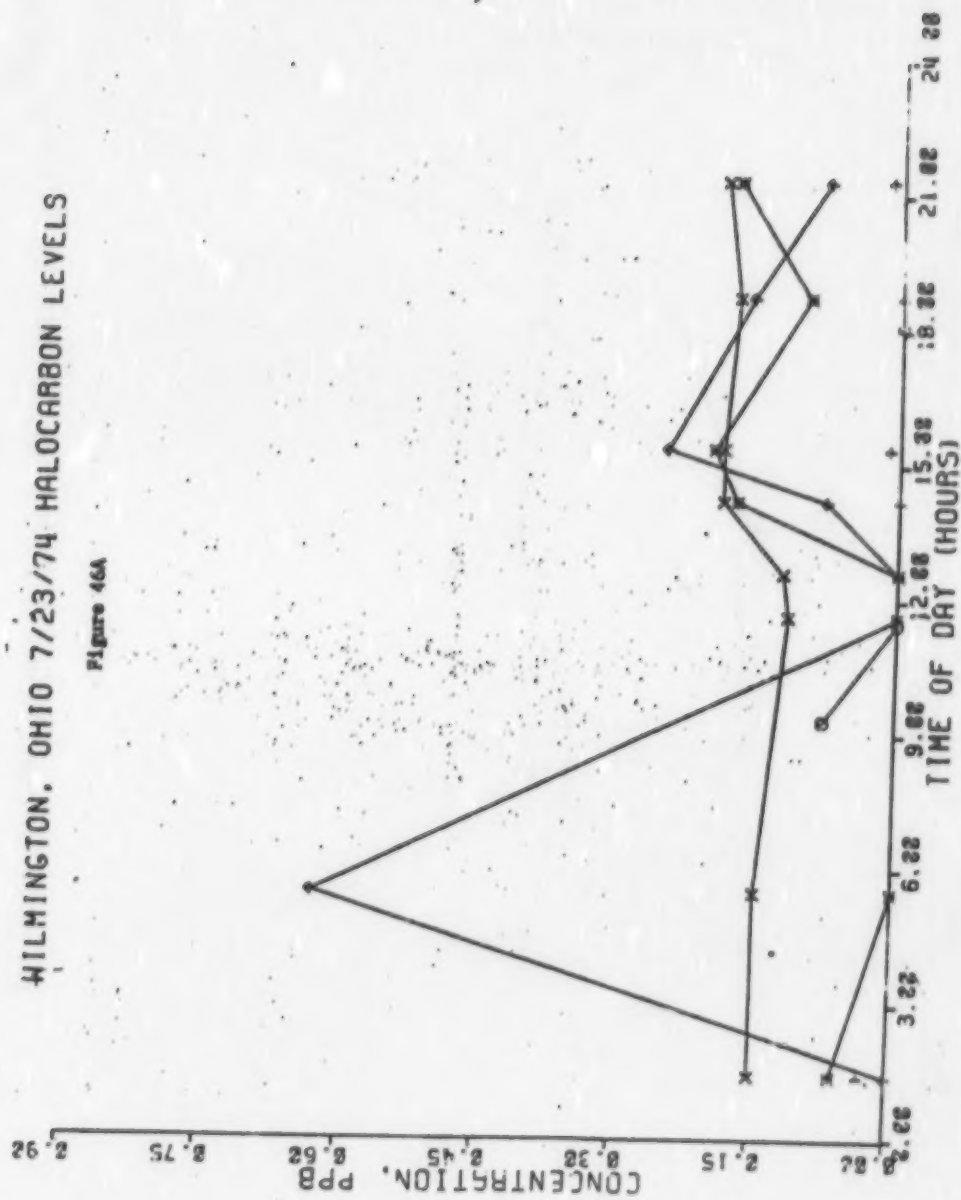
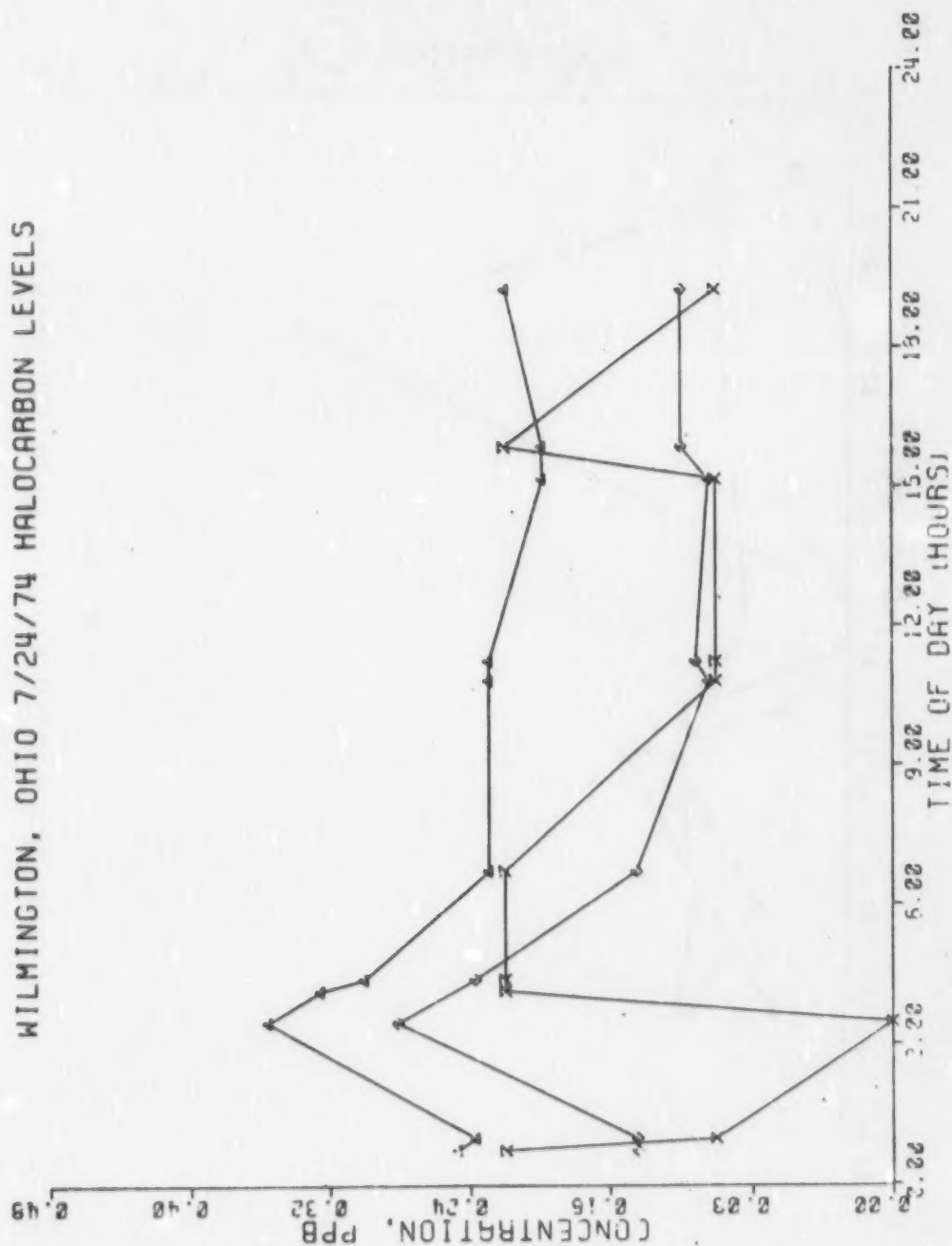


Figure 47
WILMINGTON, OHIO 7/24/74 HALOCARBON LEVELS



WILMINGTON, OHIO 7/24/74 HALOCARBON LEVELS

Figure 47A

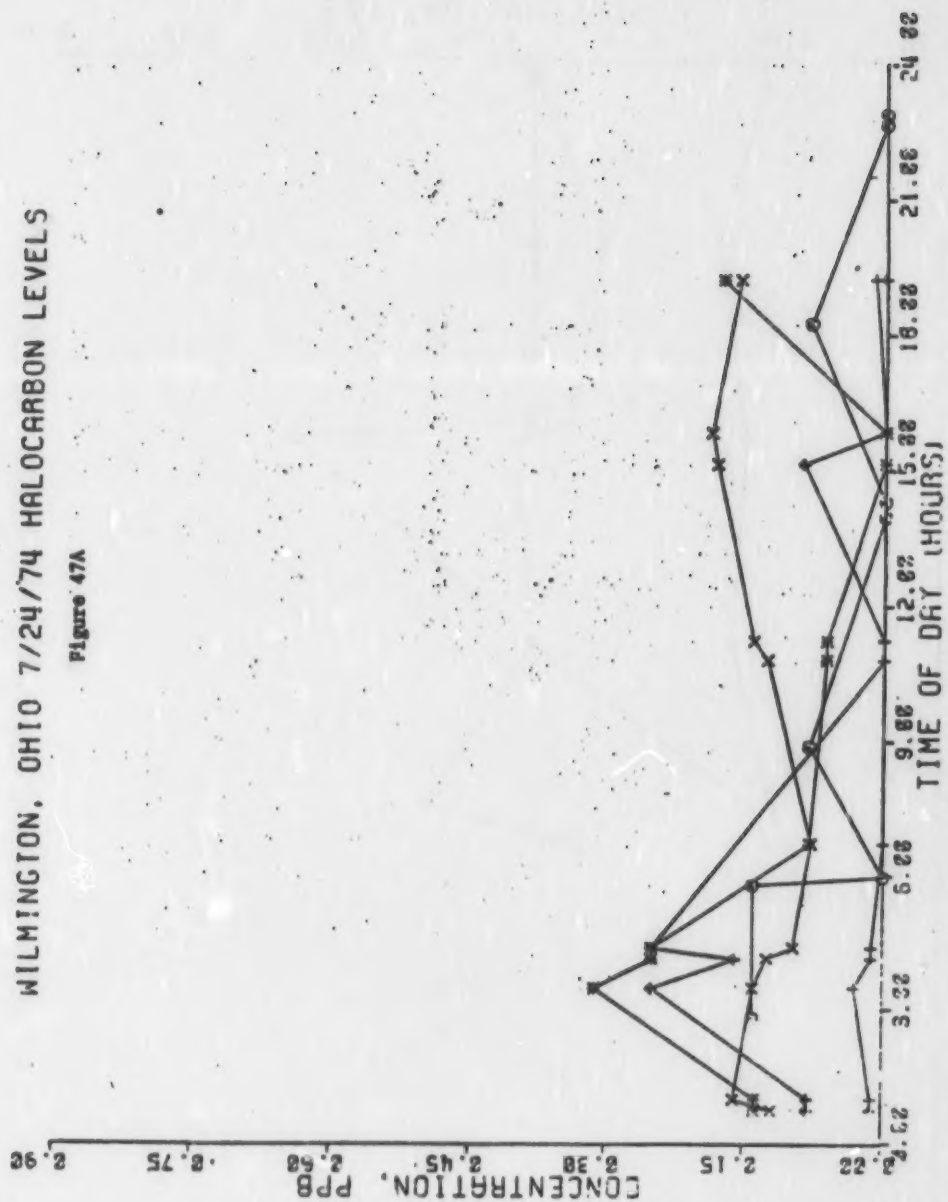
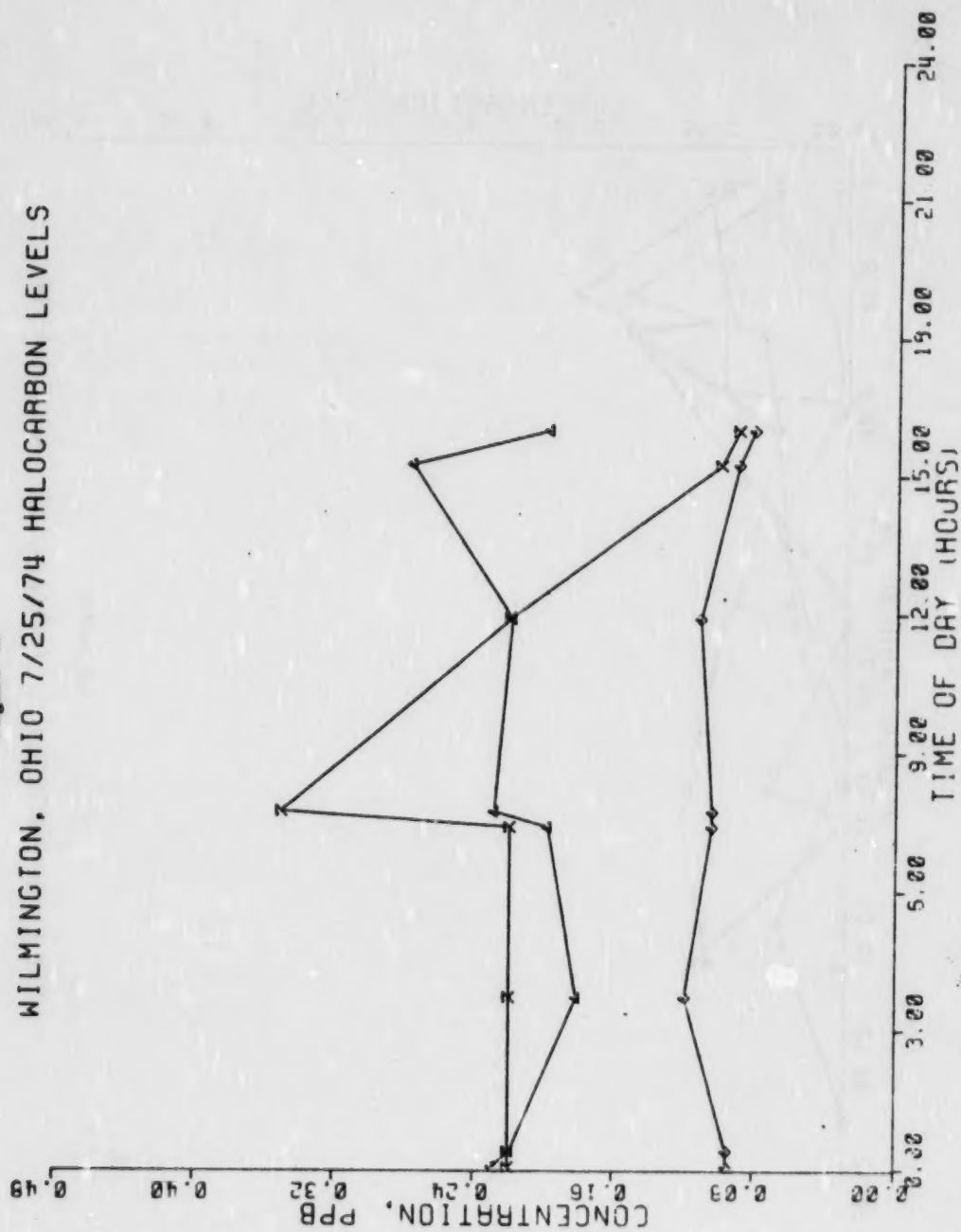


Figure 48
WILMINGTON, OHIO 7/25/74 HALOCARBON LEVELS



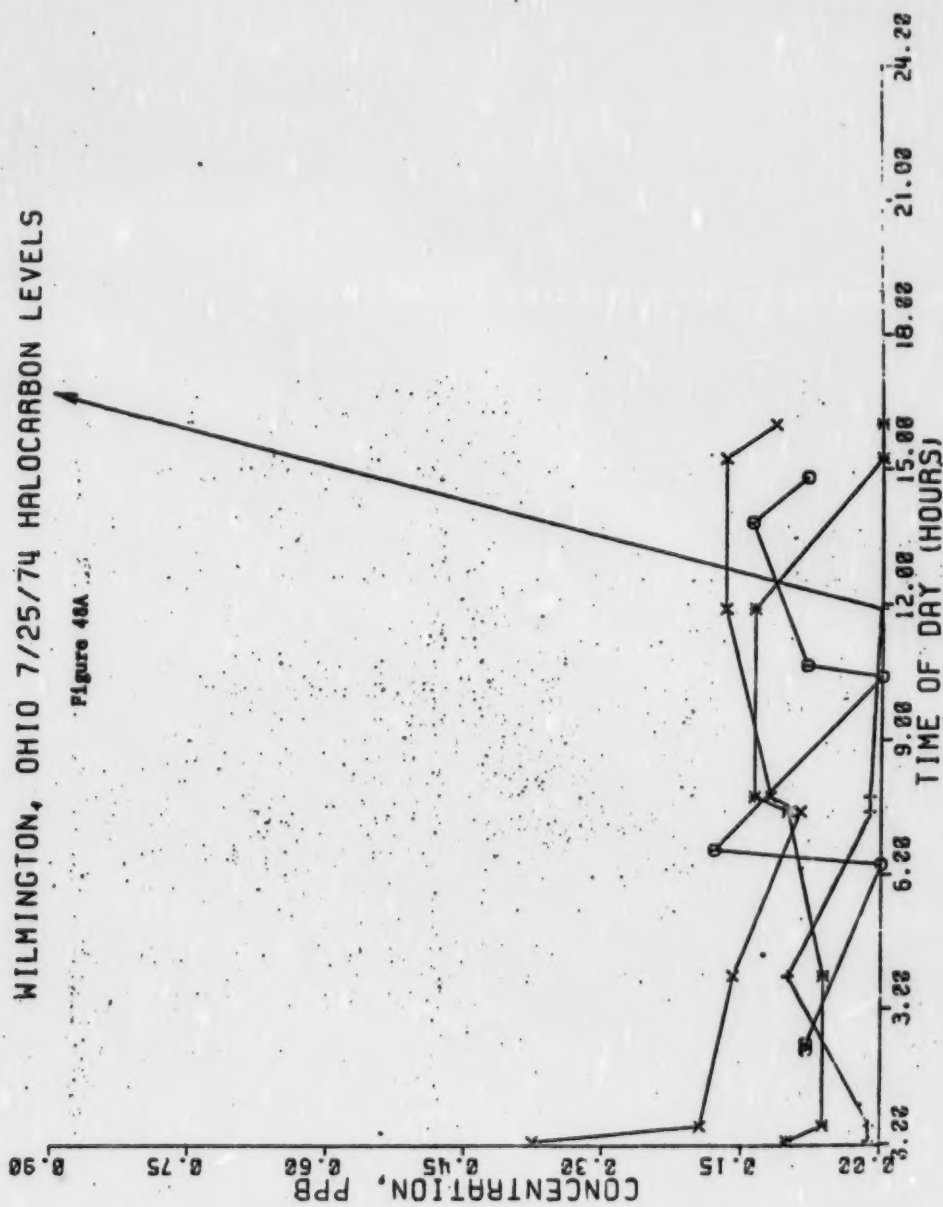
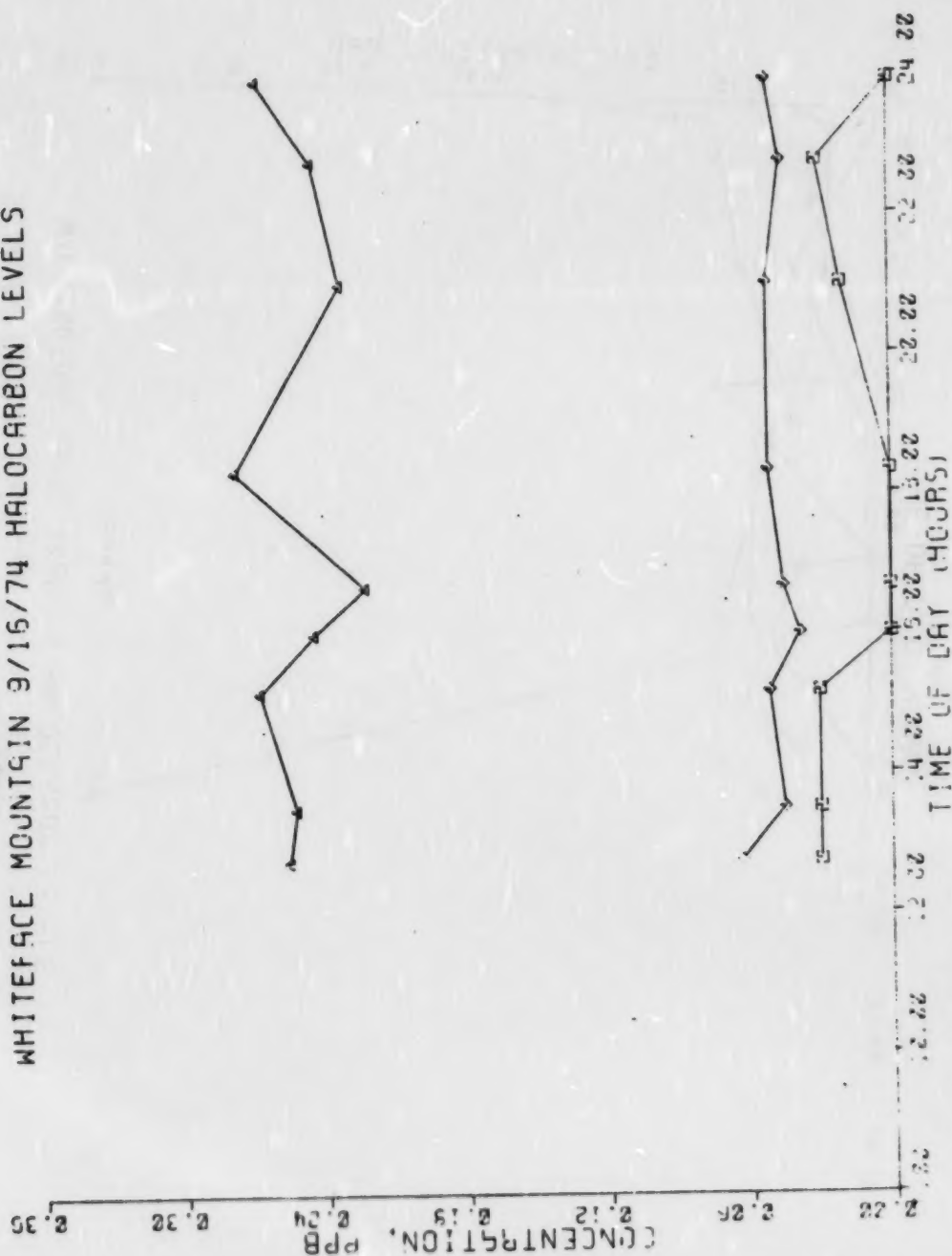


Figure 49
WHITEFACE MOUNTAIN 9/16/74 HALOCARBON LEVELS



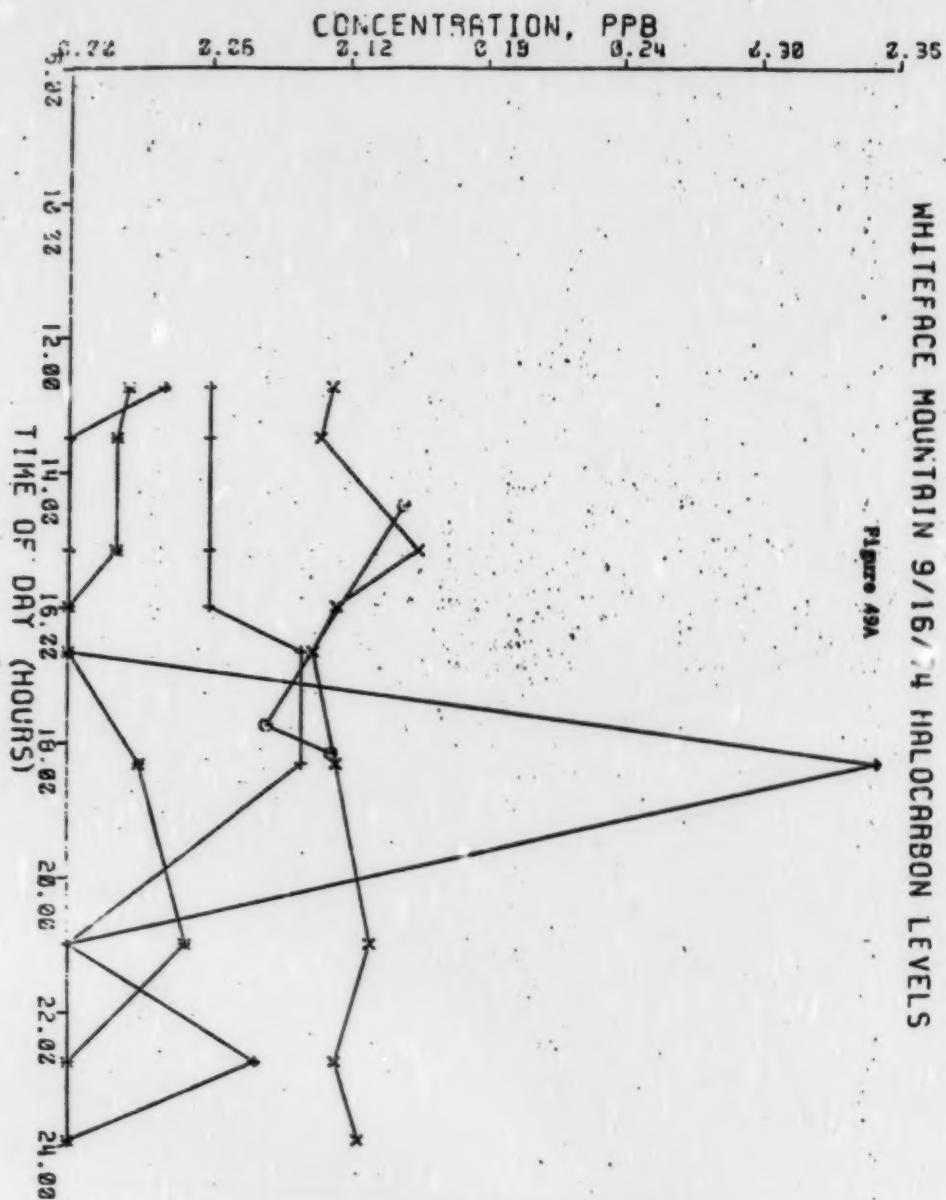
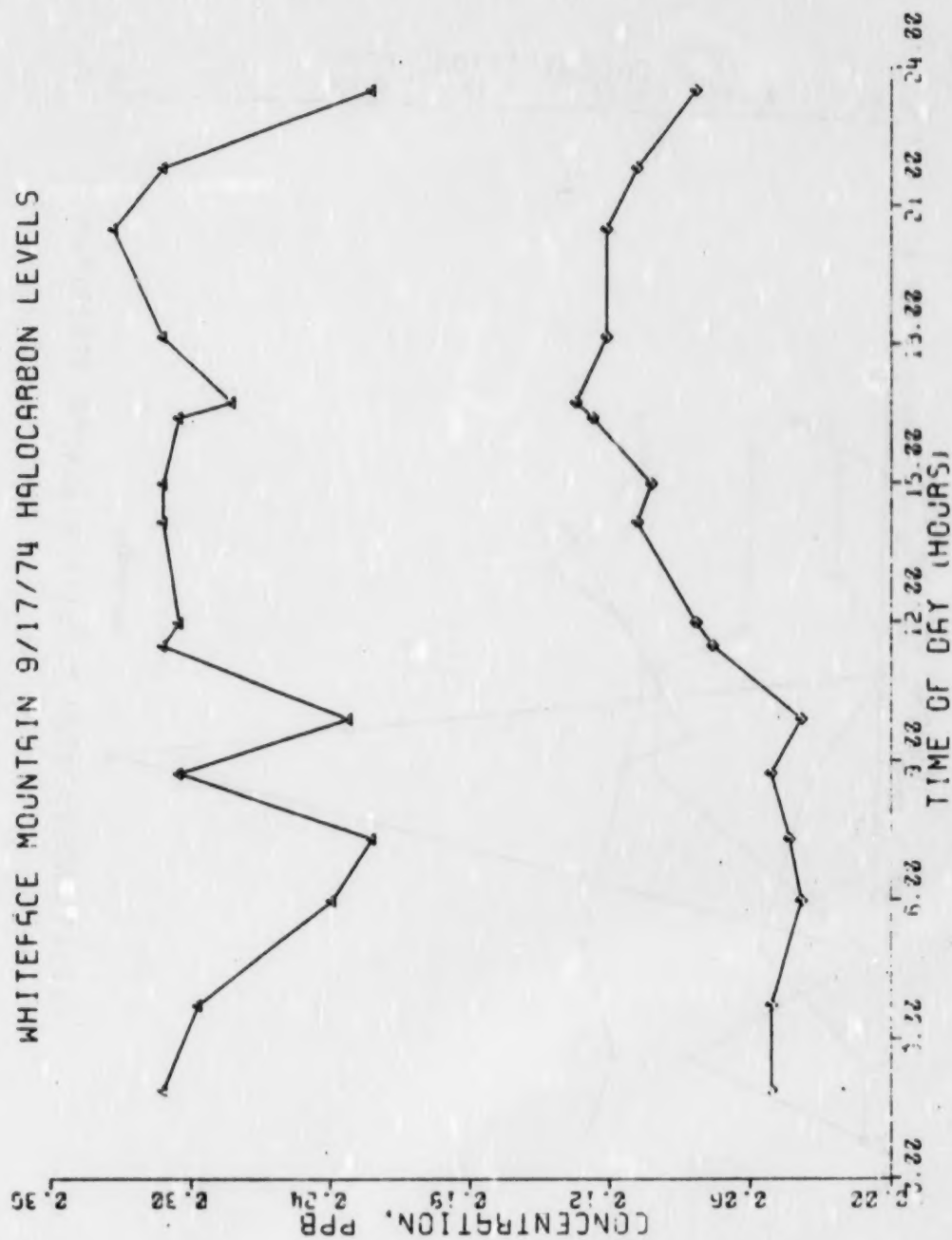


Figure 50

WHITEFACE MOUNTAIN 9/17/74 HALOCARBON LEVELS



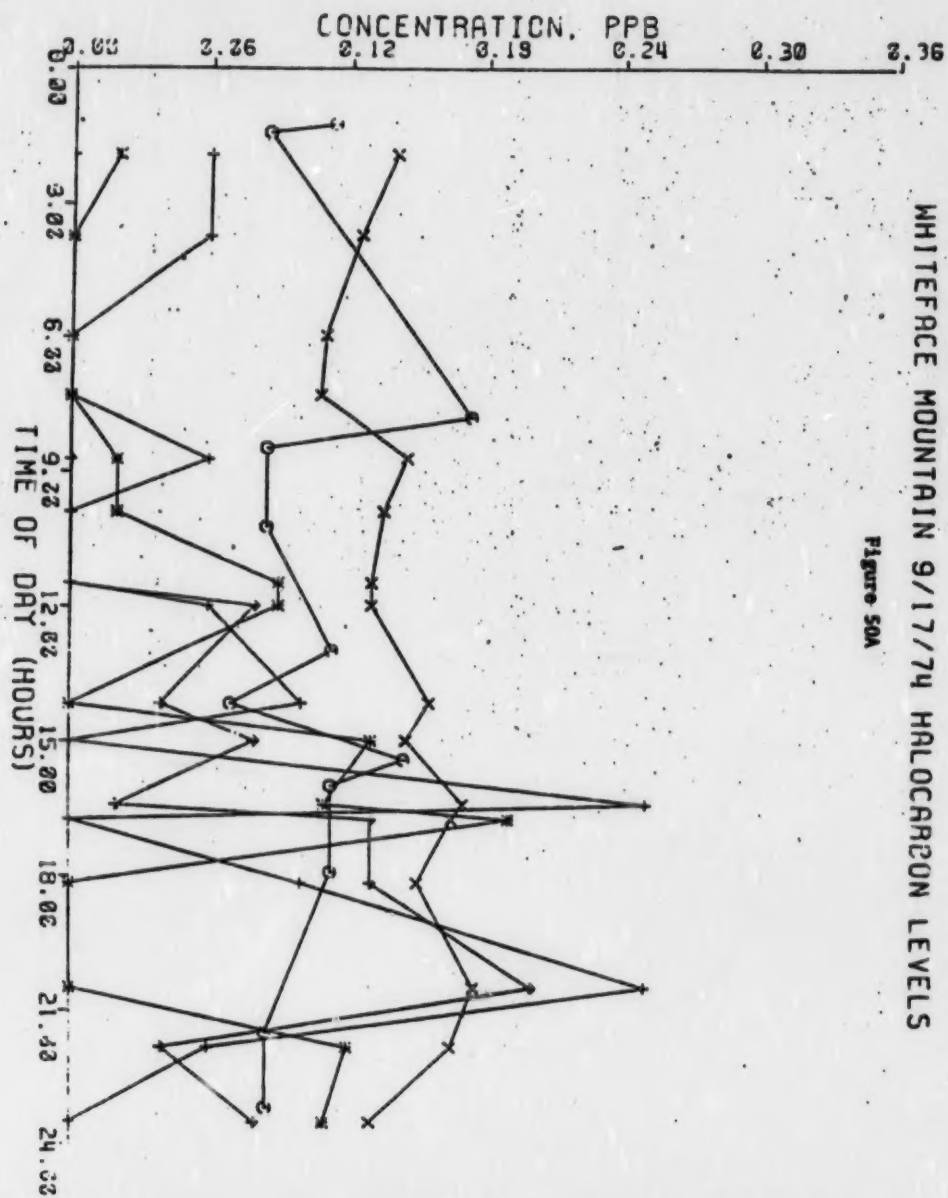
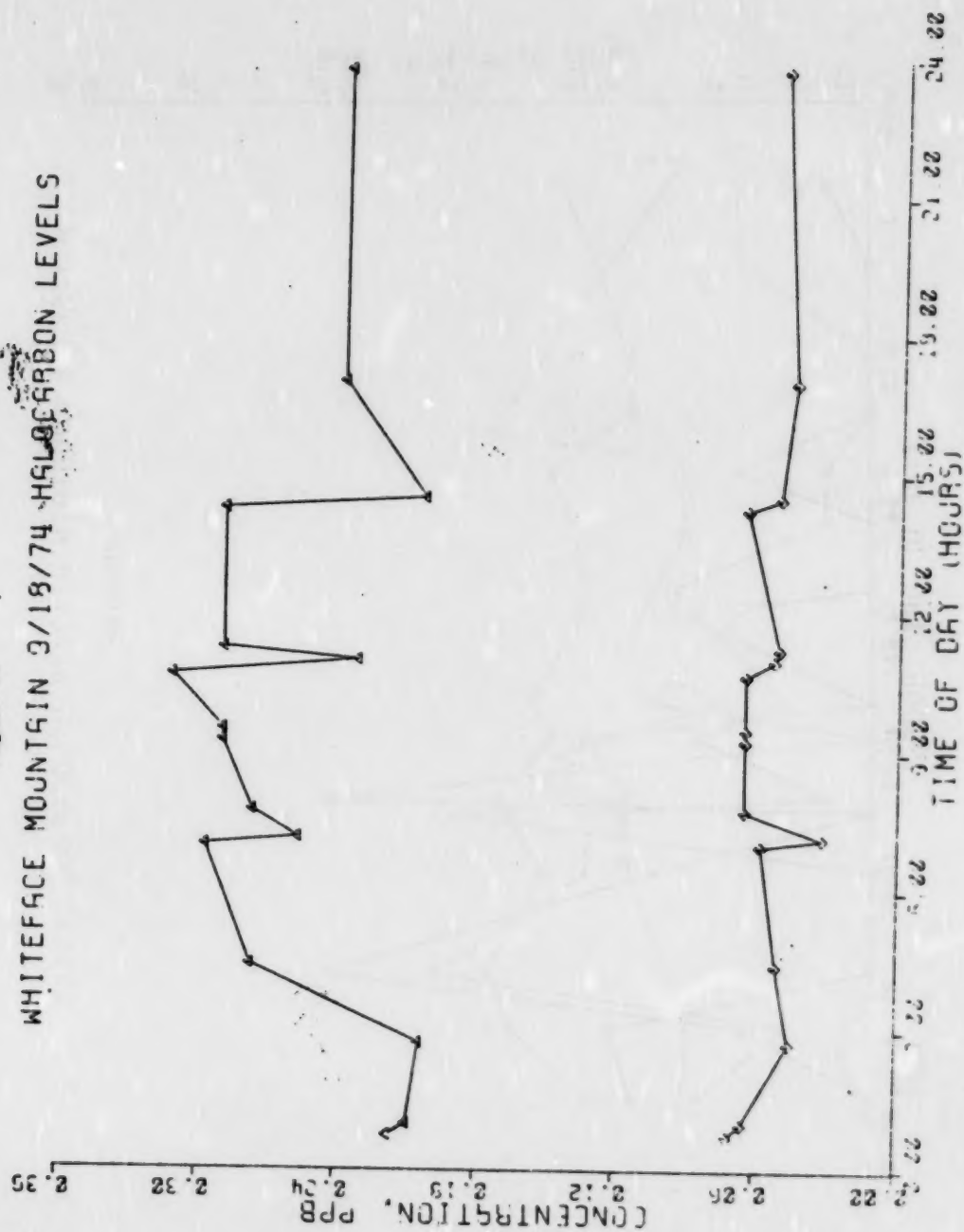


Figure 51
WHITEFACE MOUNTAIN 3/18/74 HALOCARBON LEVELS



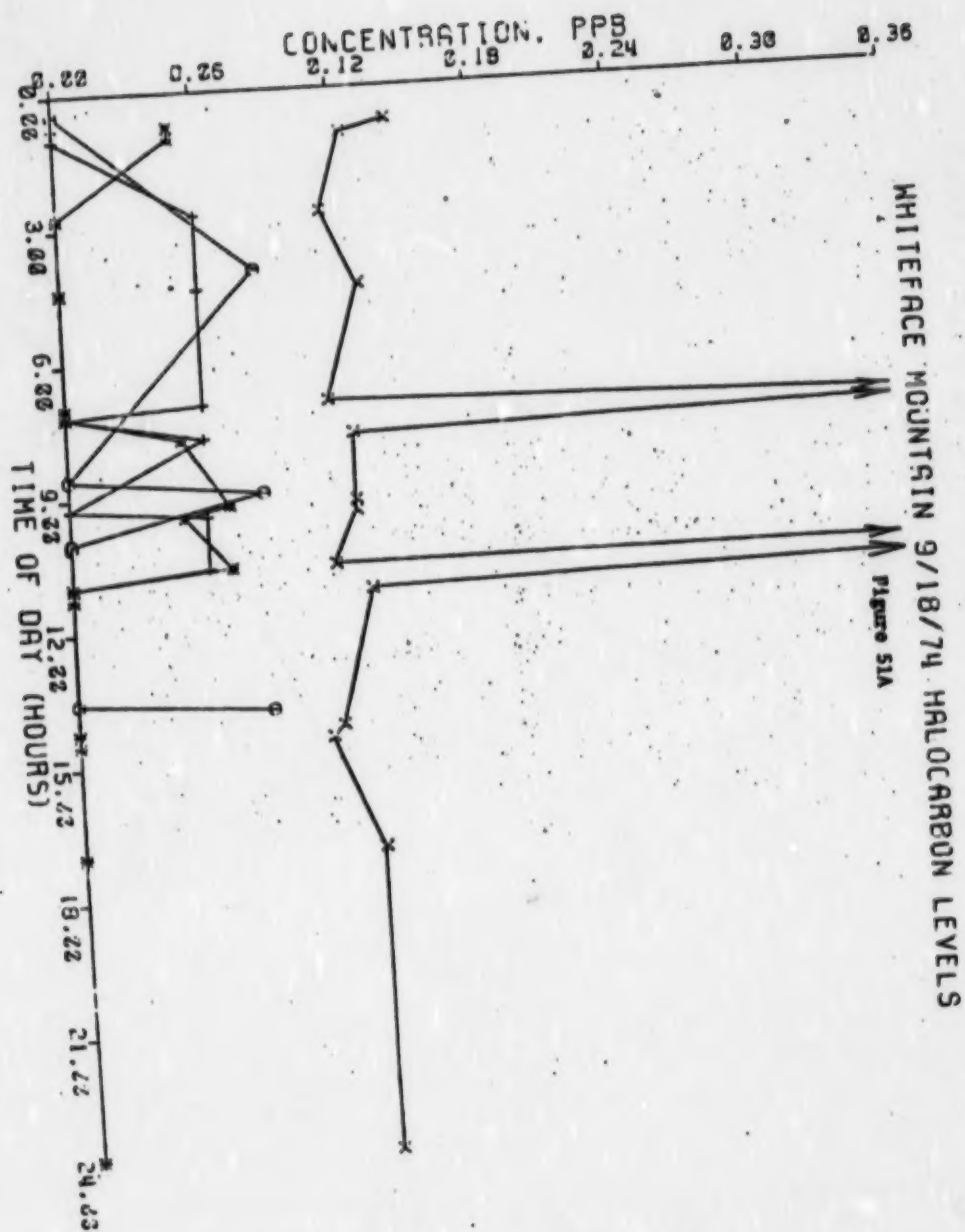
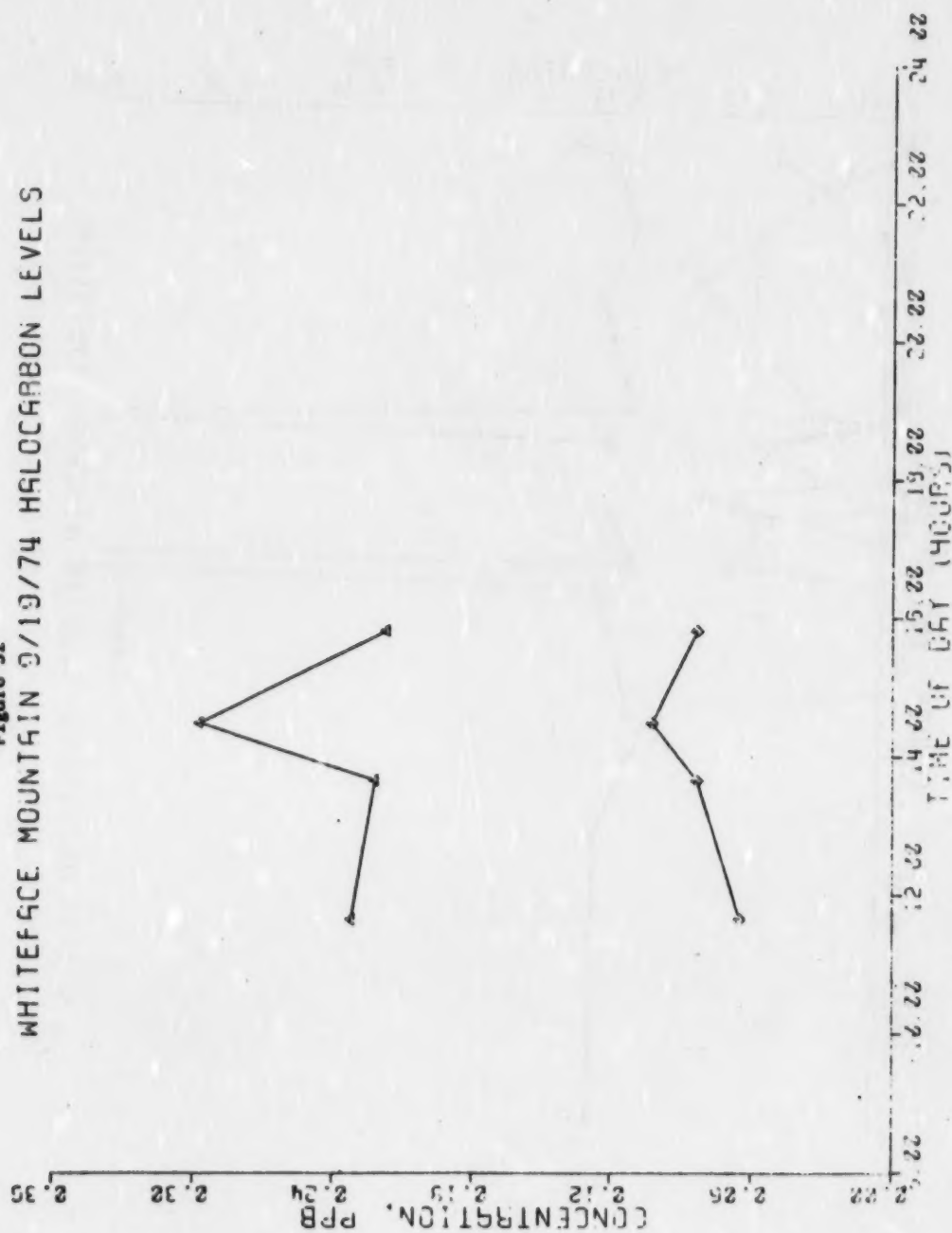
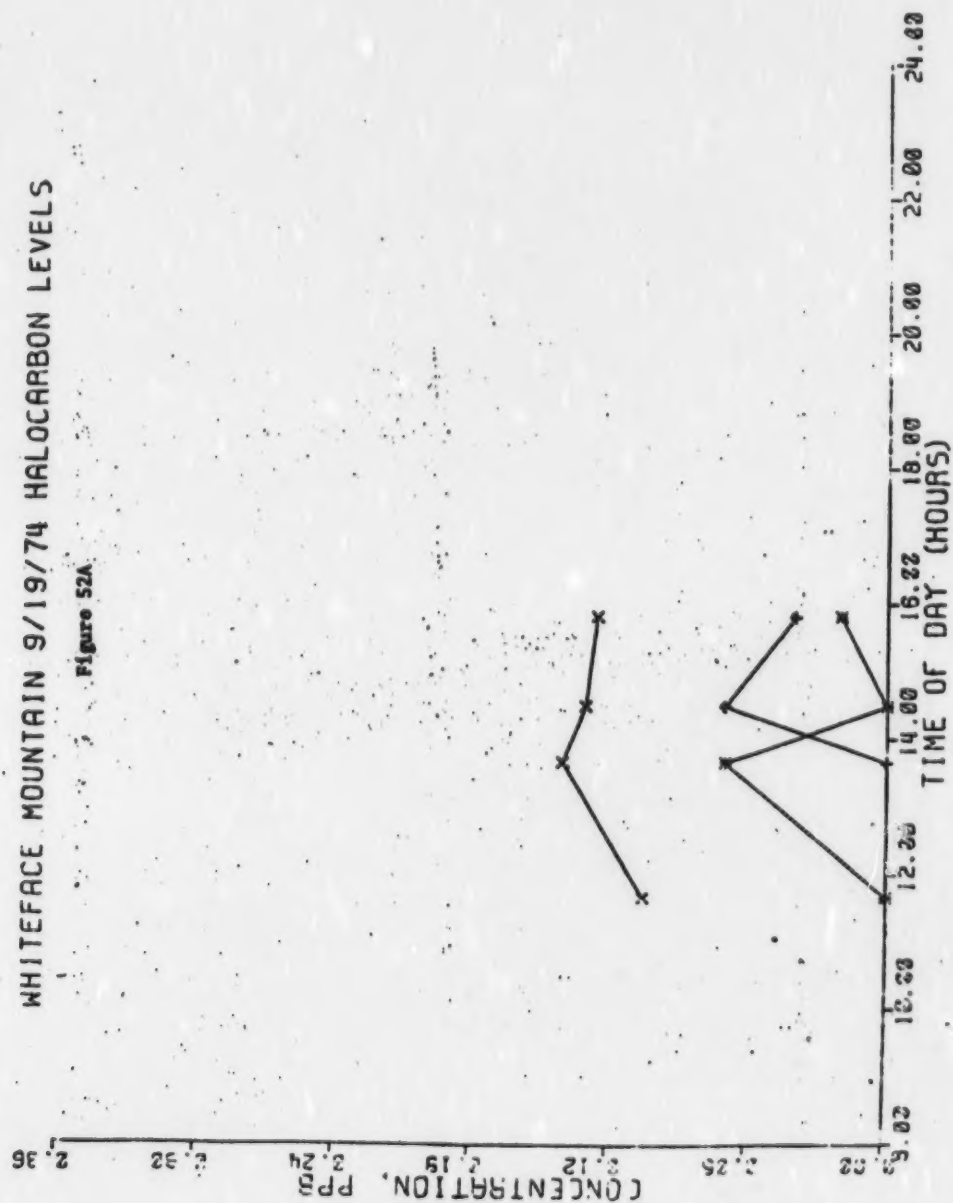


Figure 52
WHITEFACE MOUNTAIN 9/19/74 HALOCARBON LEVELS



WHITEFACE MOUNTAIN 9/19/74 HALOCARBON LEVELS

Figure 52A



PPB OR MICROGRAMS/CUB
12.02 12.02 12.02



Figure 54
SEACIAT 6/19/74 AMBIENT DATA

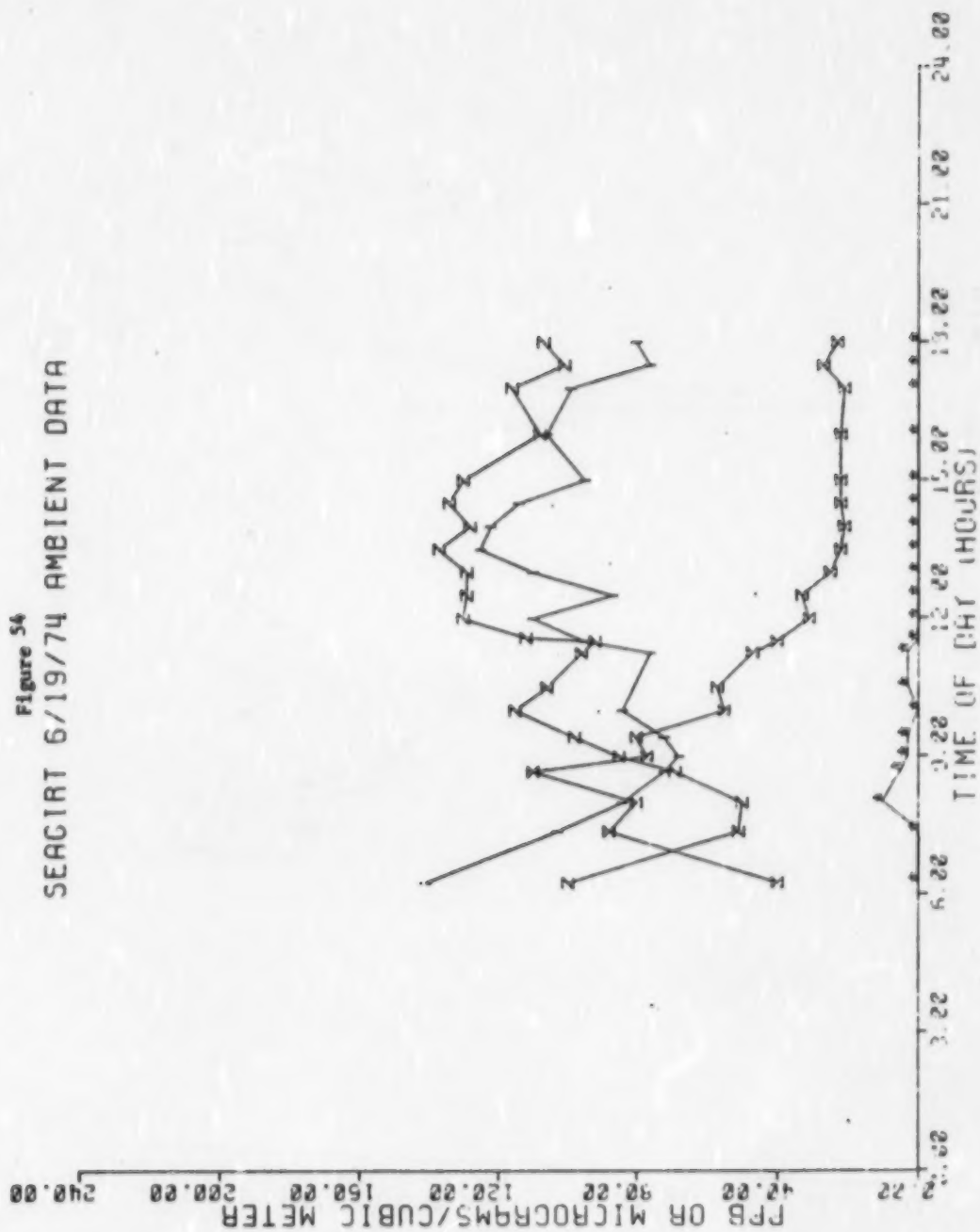


Figure 55.
NEW YORK CITY 5/27/74 AMBIENT DATA

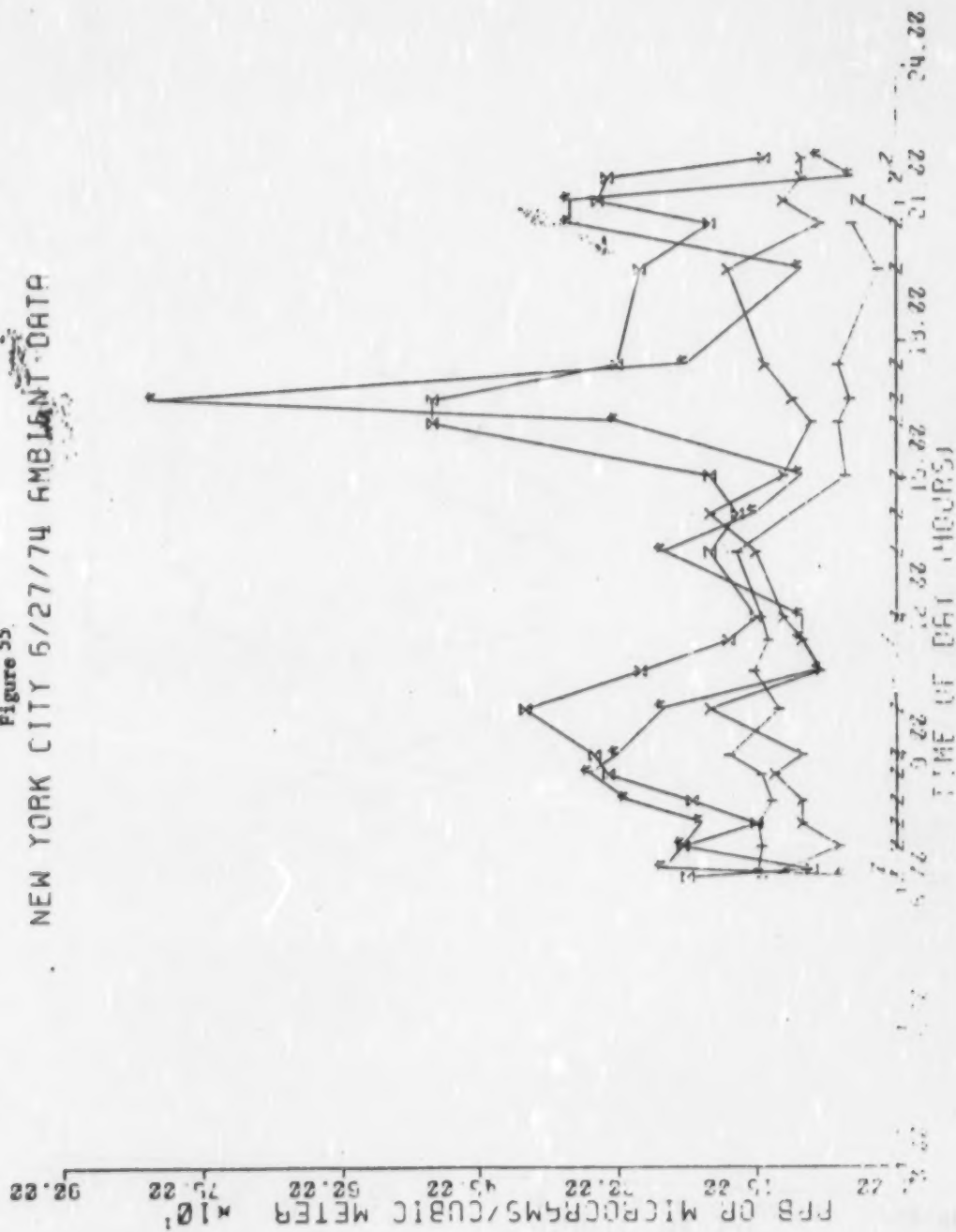
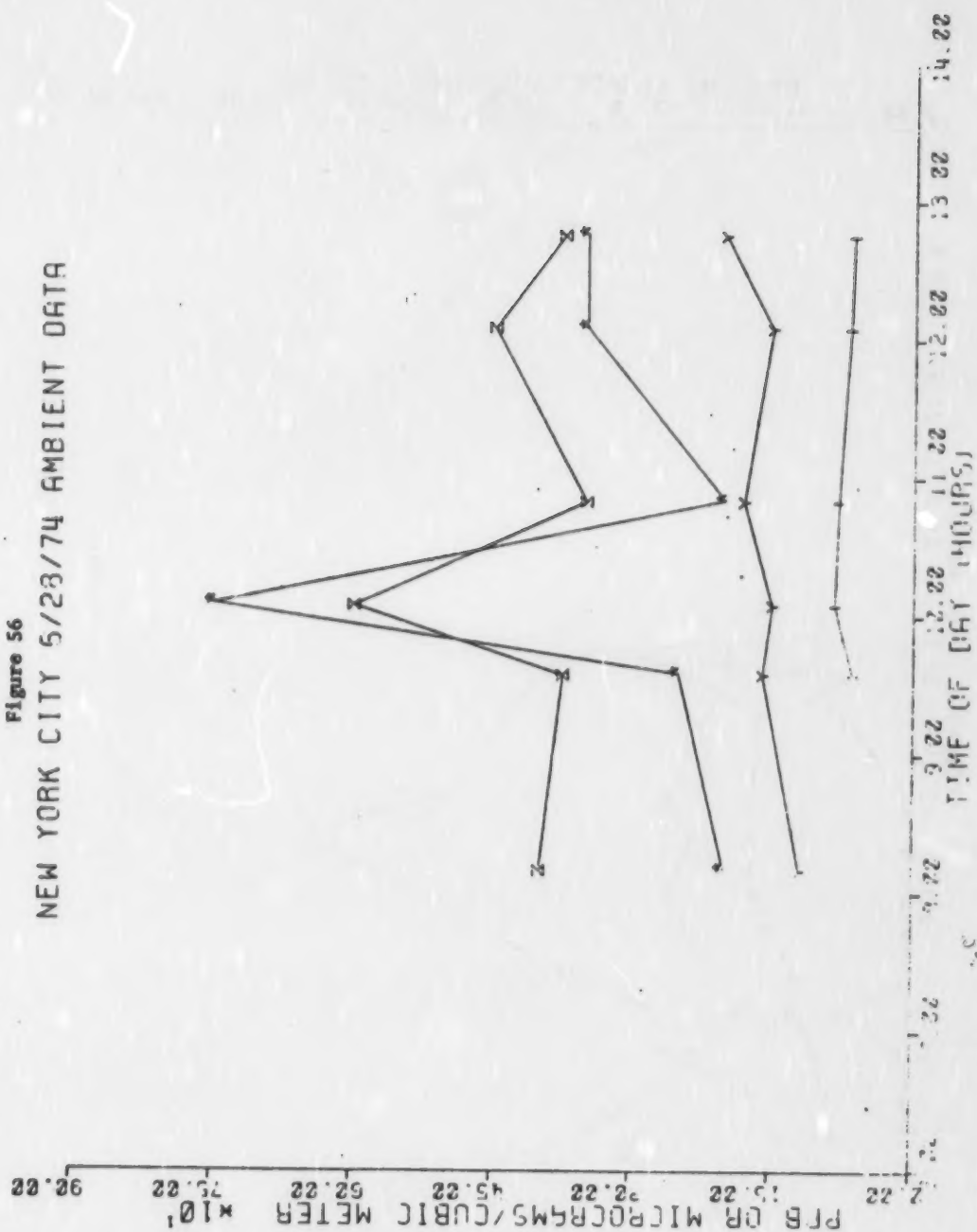


Figure 56
NEW YORK CITY 5/23/74 AMBIENT DATA



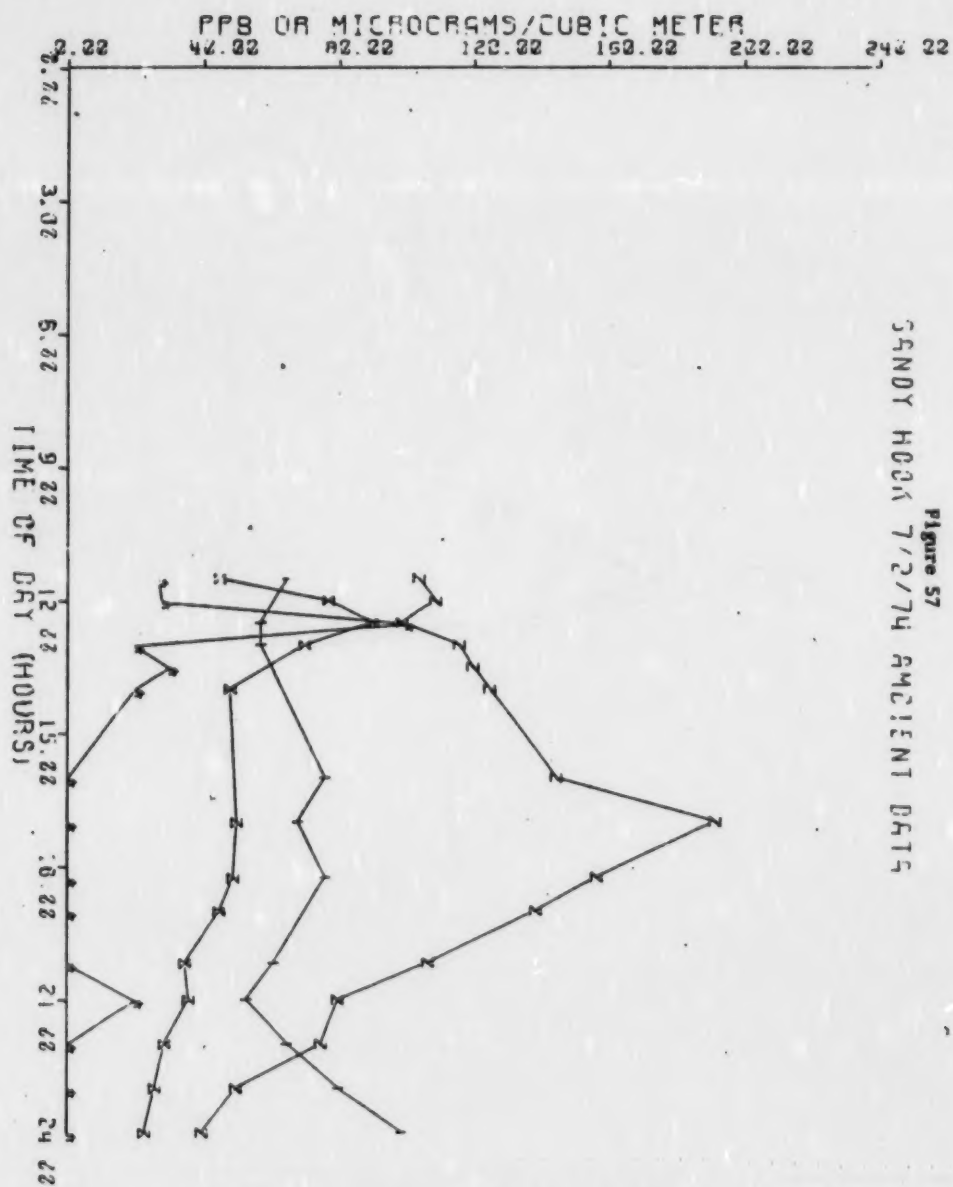


Figure 57
SANDY HOOK 7/2/74 AMBIENT DATA

Figure 58
SANDY HOOK 7/3/74 AMBIENT DATA

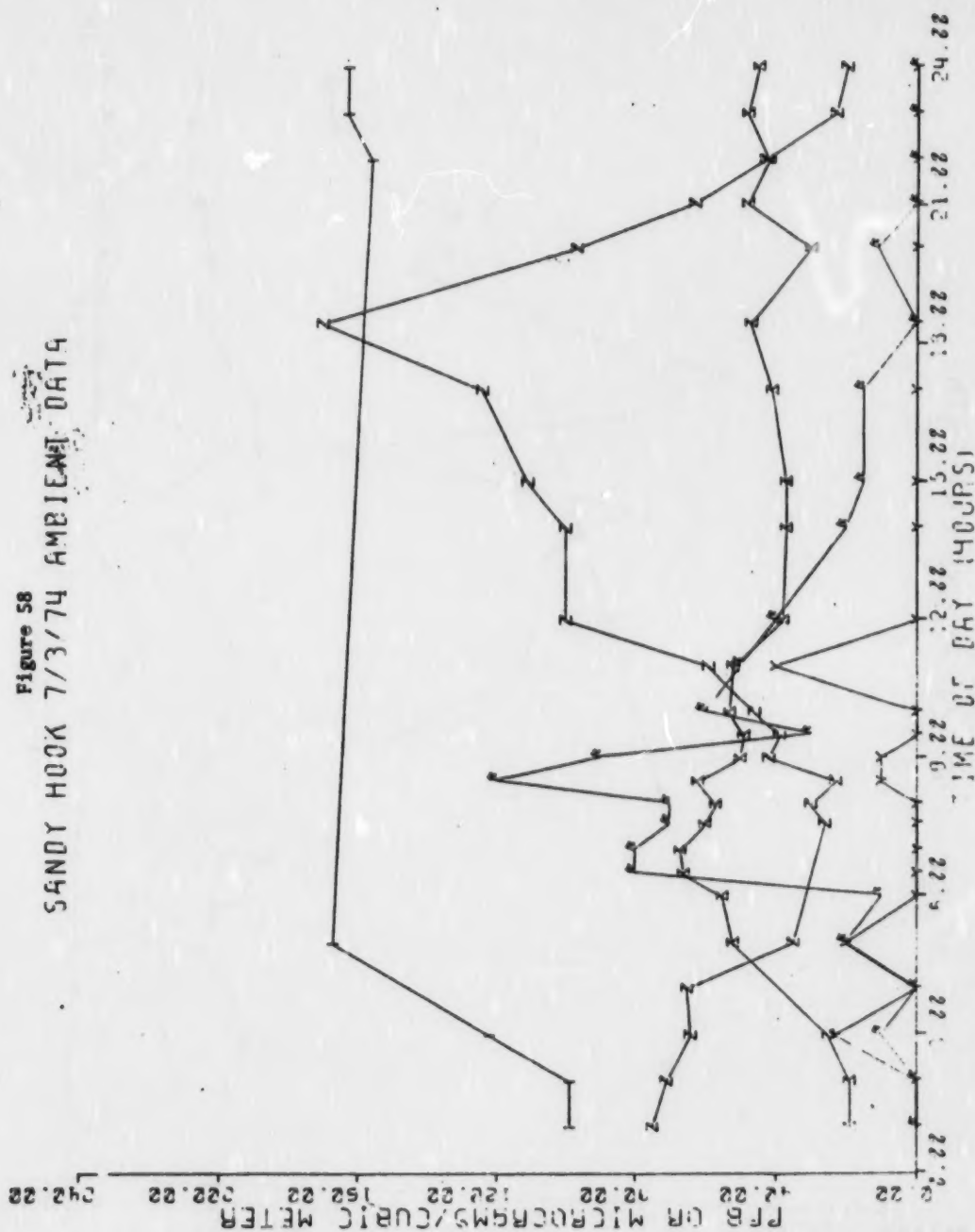


Figure 59
SANDY HOOK 7/4/74 AMBIENT DATA

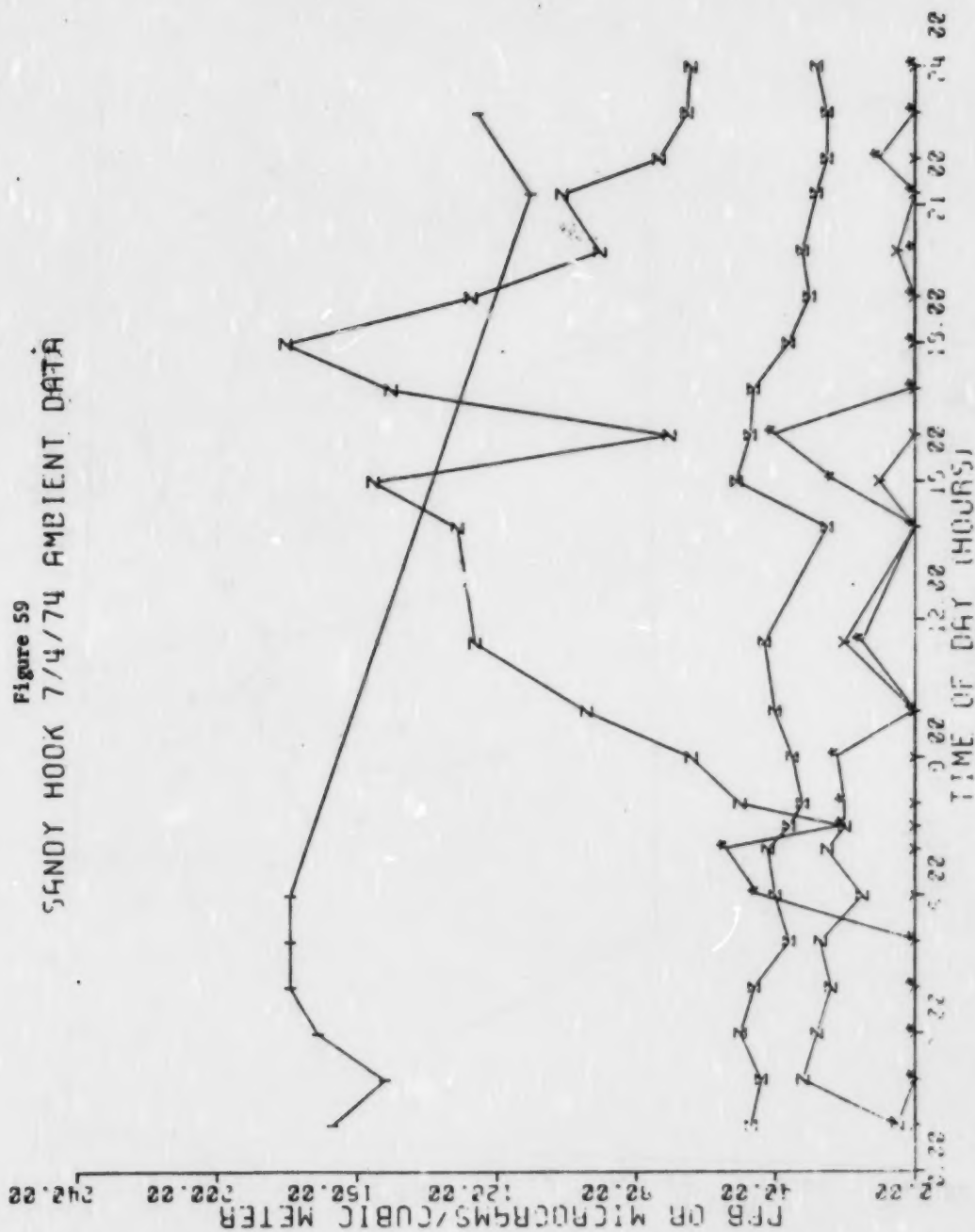
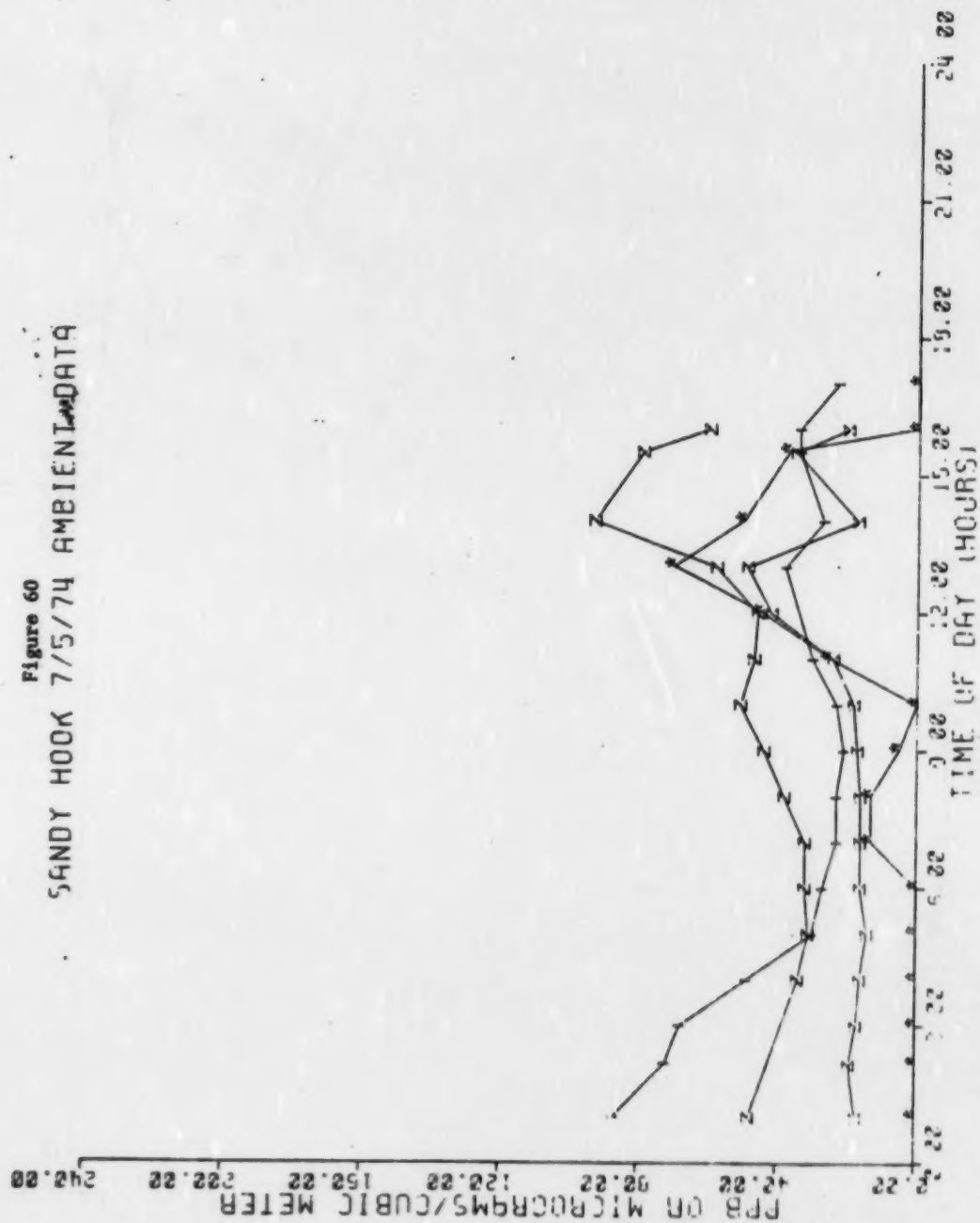


Figure 60
SANDY HOOK 7/5/74 AMBIENT DATA



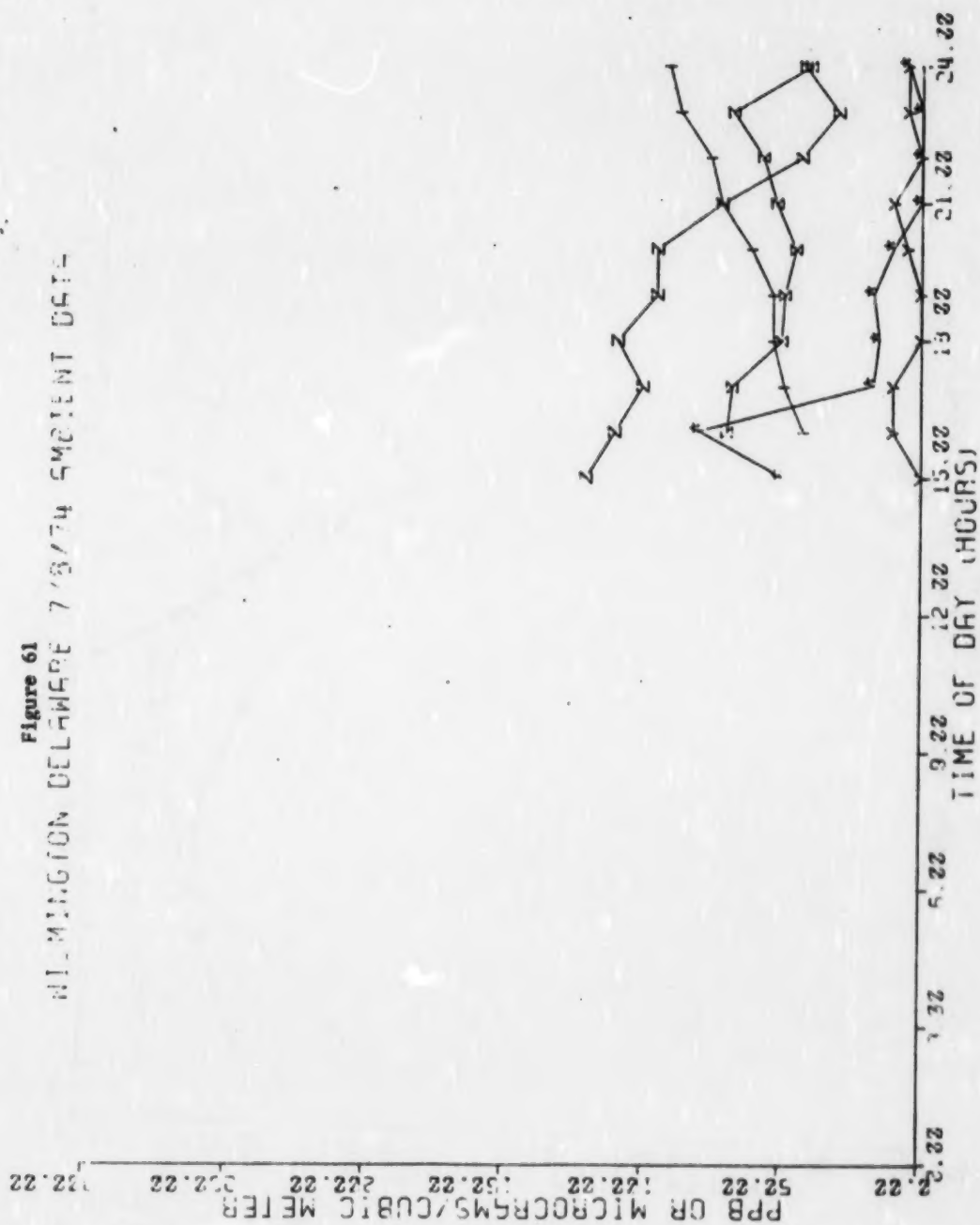
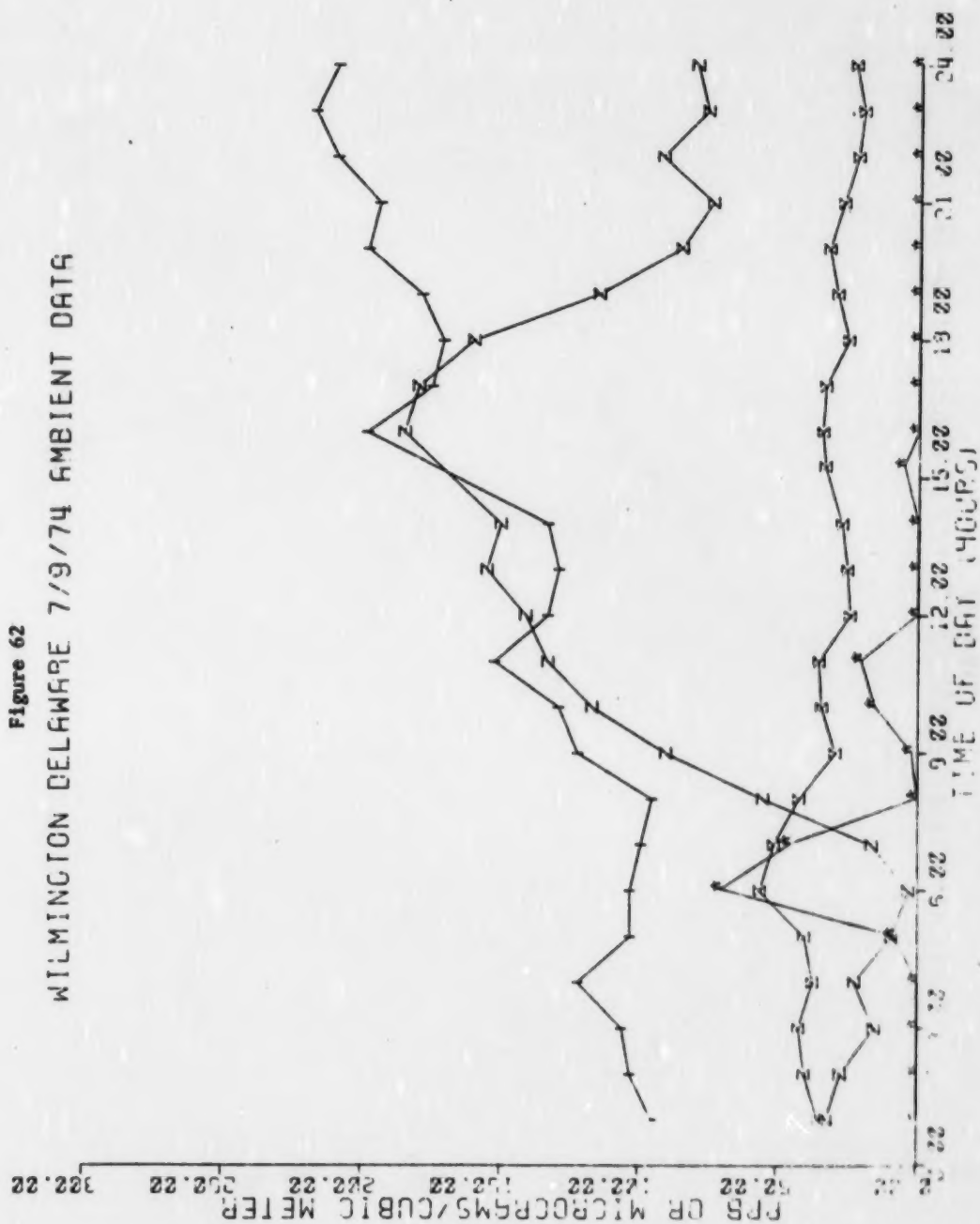
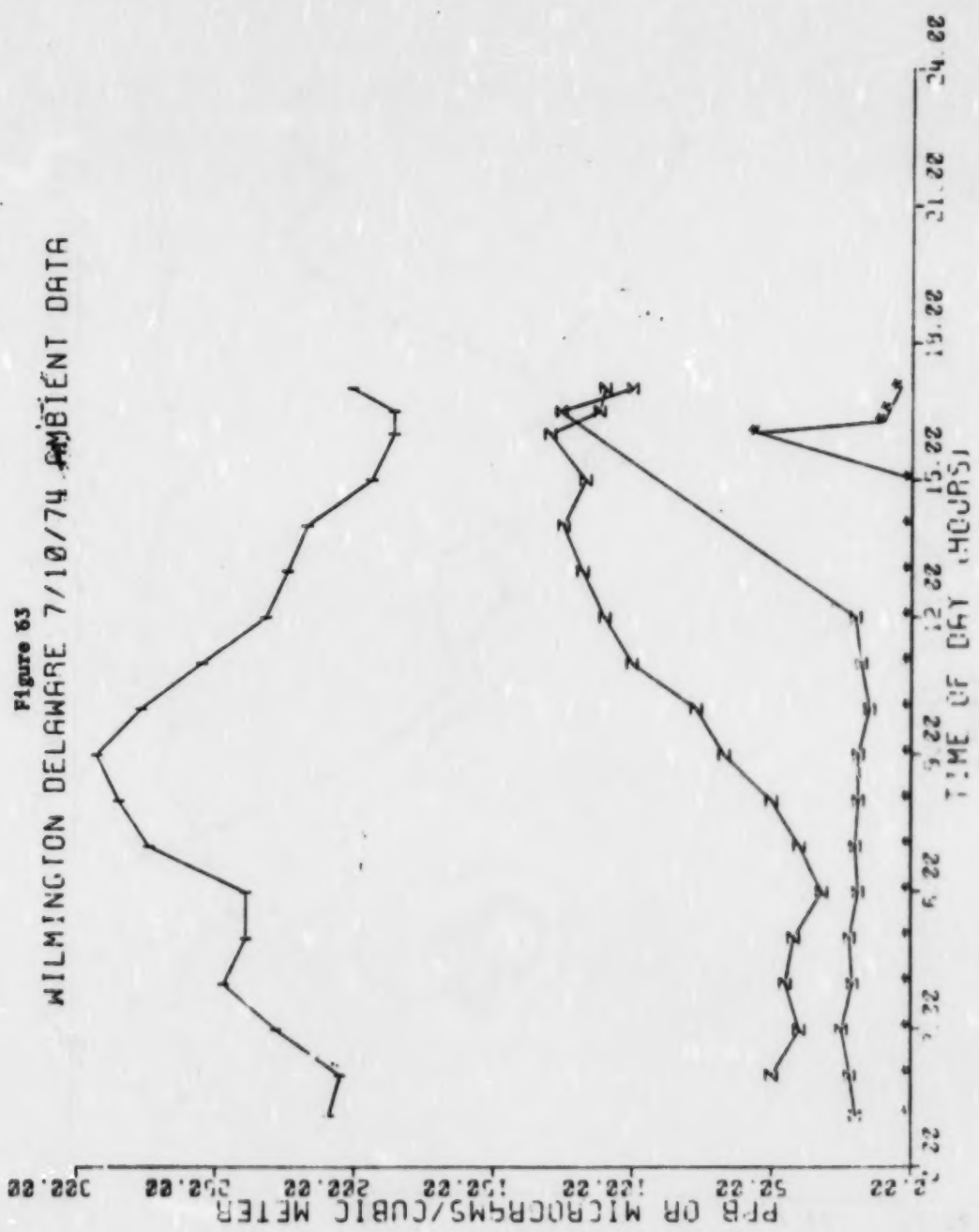


Figure 62
WILMINGTON DELAWARE 7/9/74 AMBIENT DATA





PPB OR MICROGRAMS/CUBIC METER

Figure 64
BALTIMORE, MARYLAND 7/11/74 AMBIENT DATA

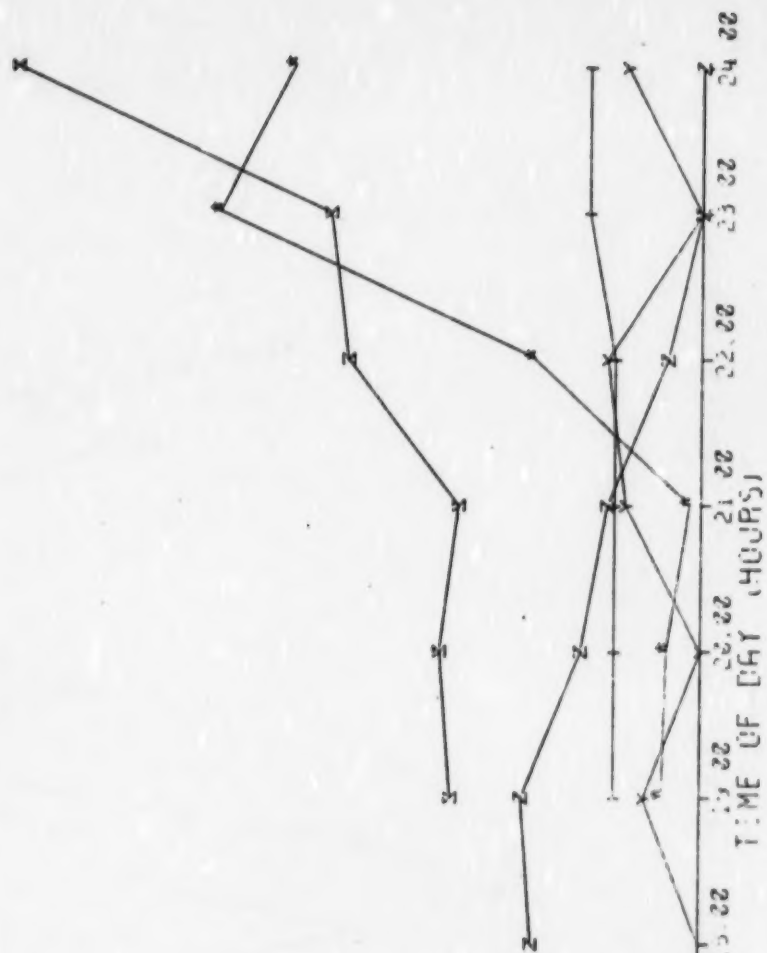


Figure 65

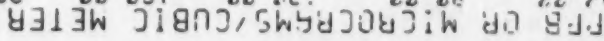
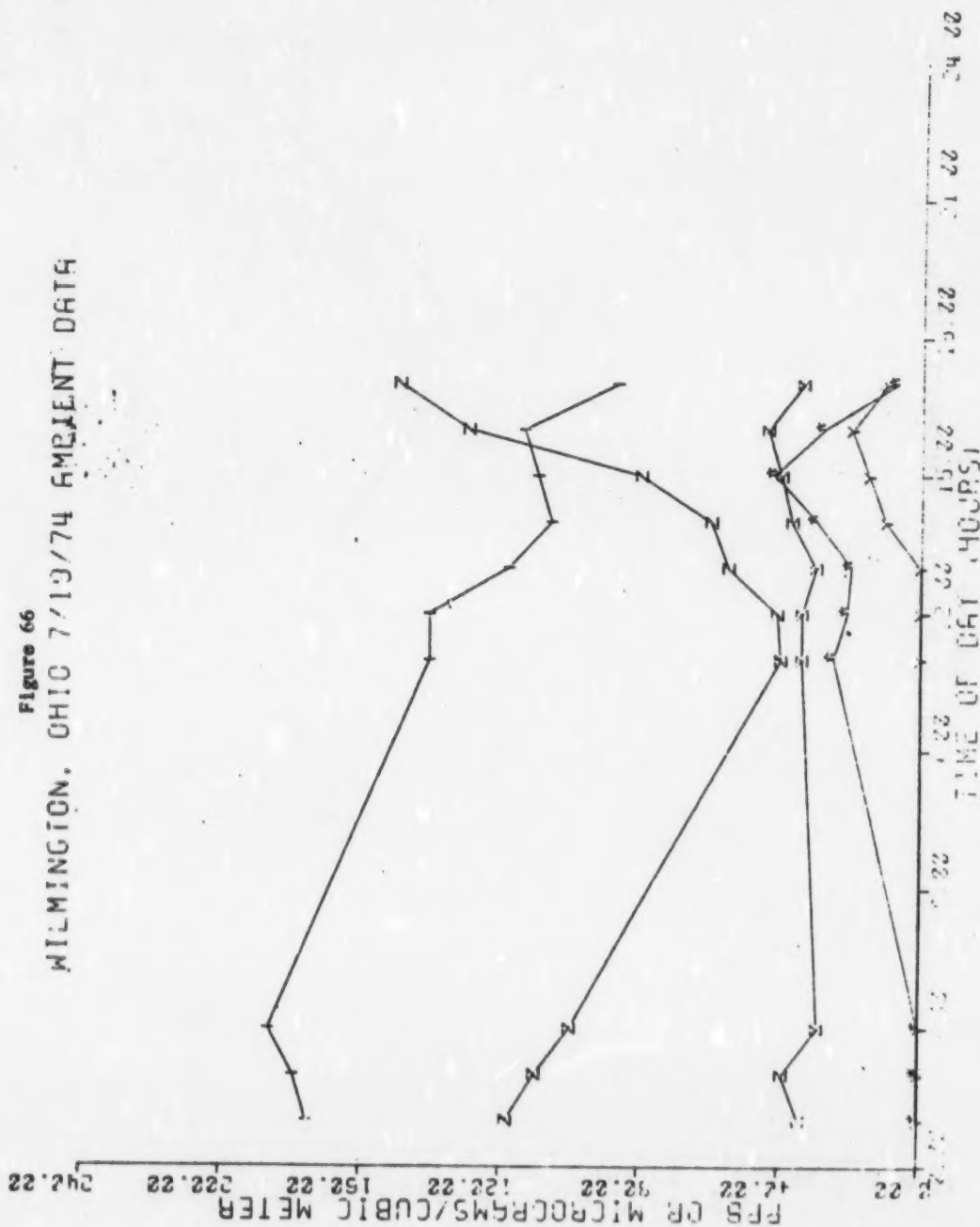
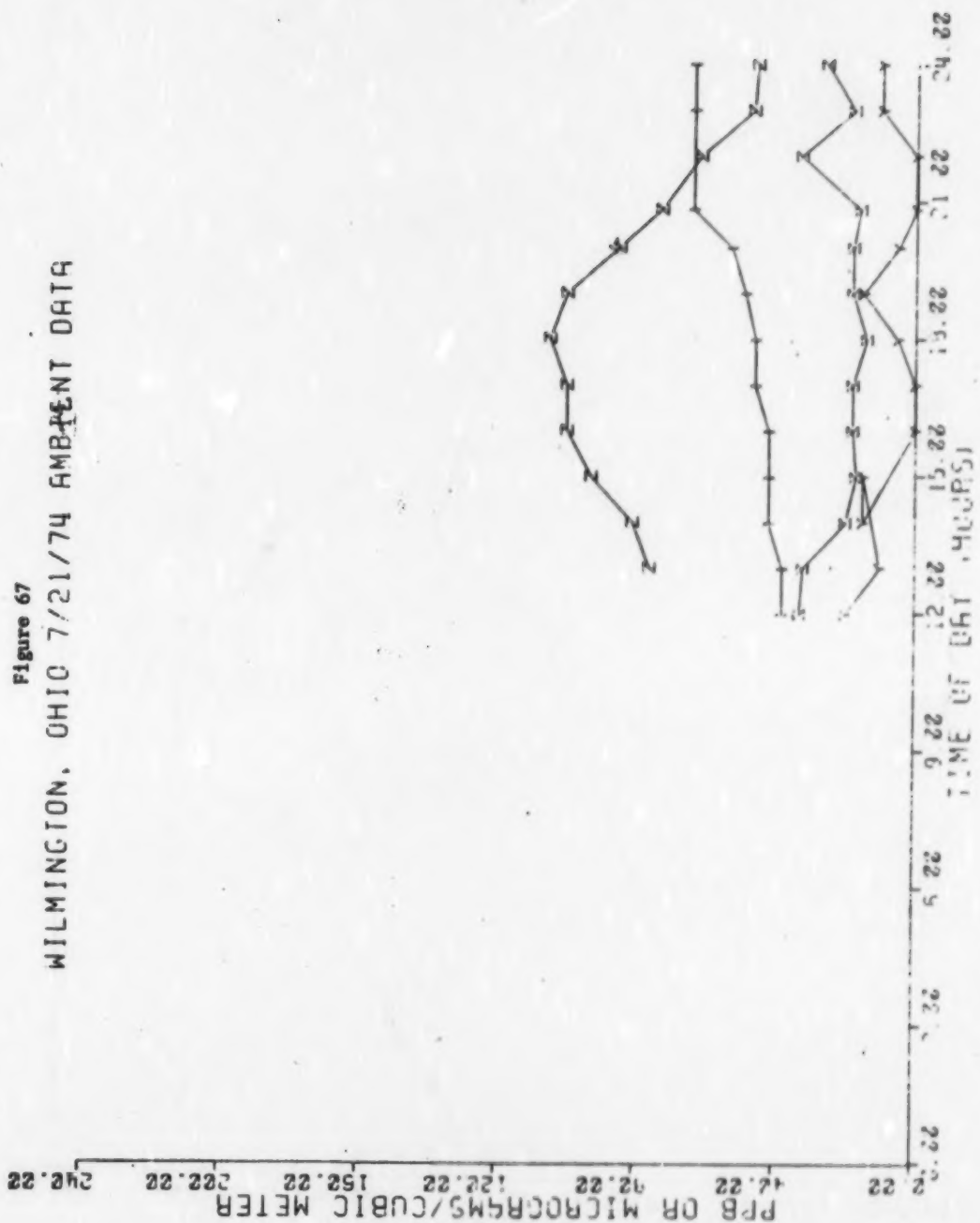
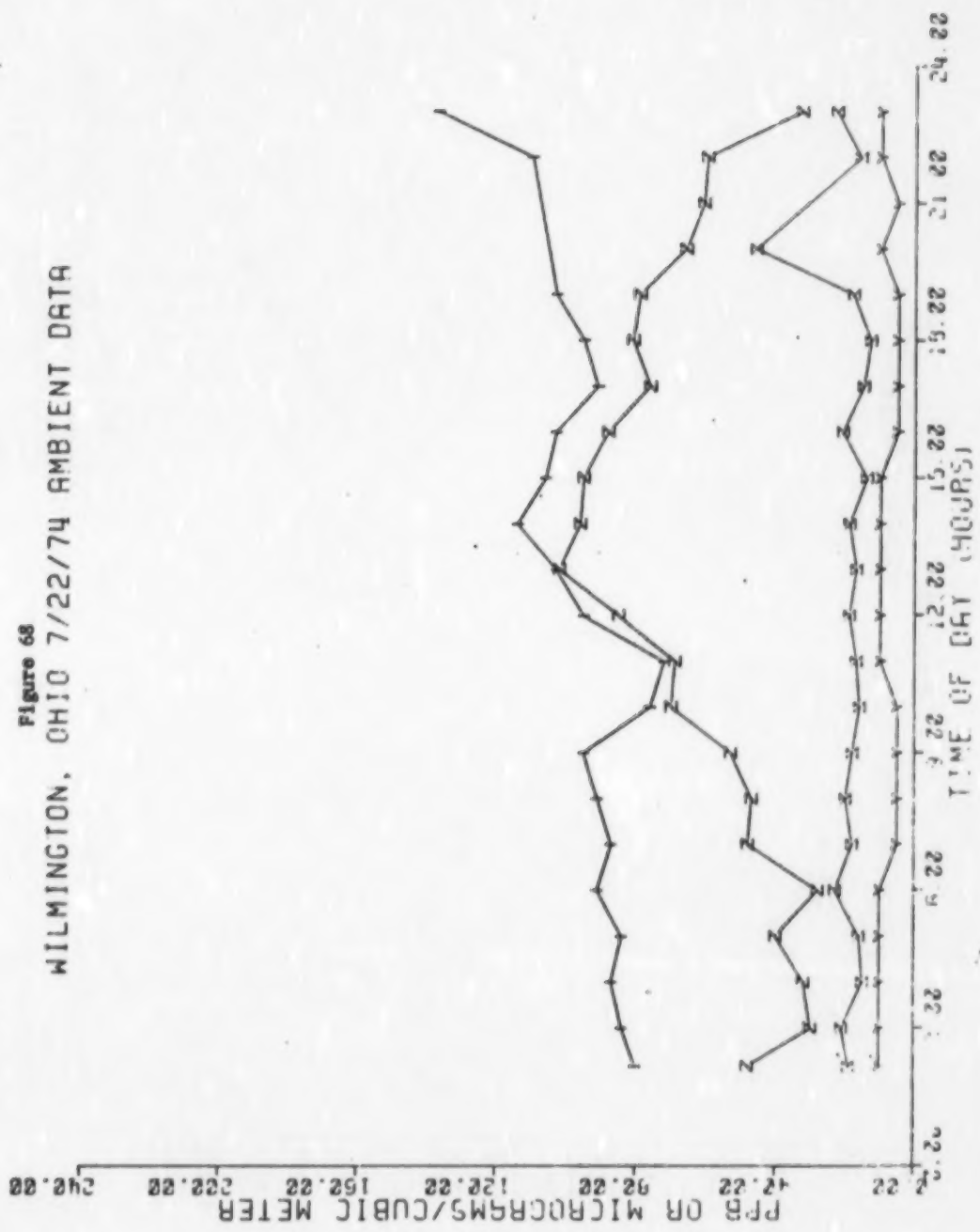
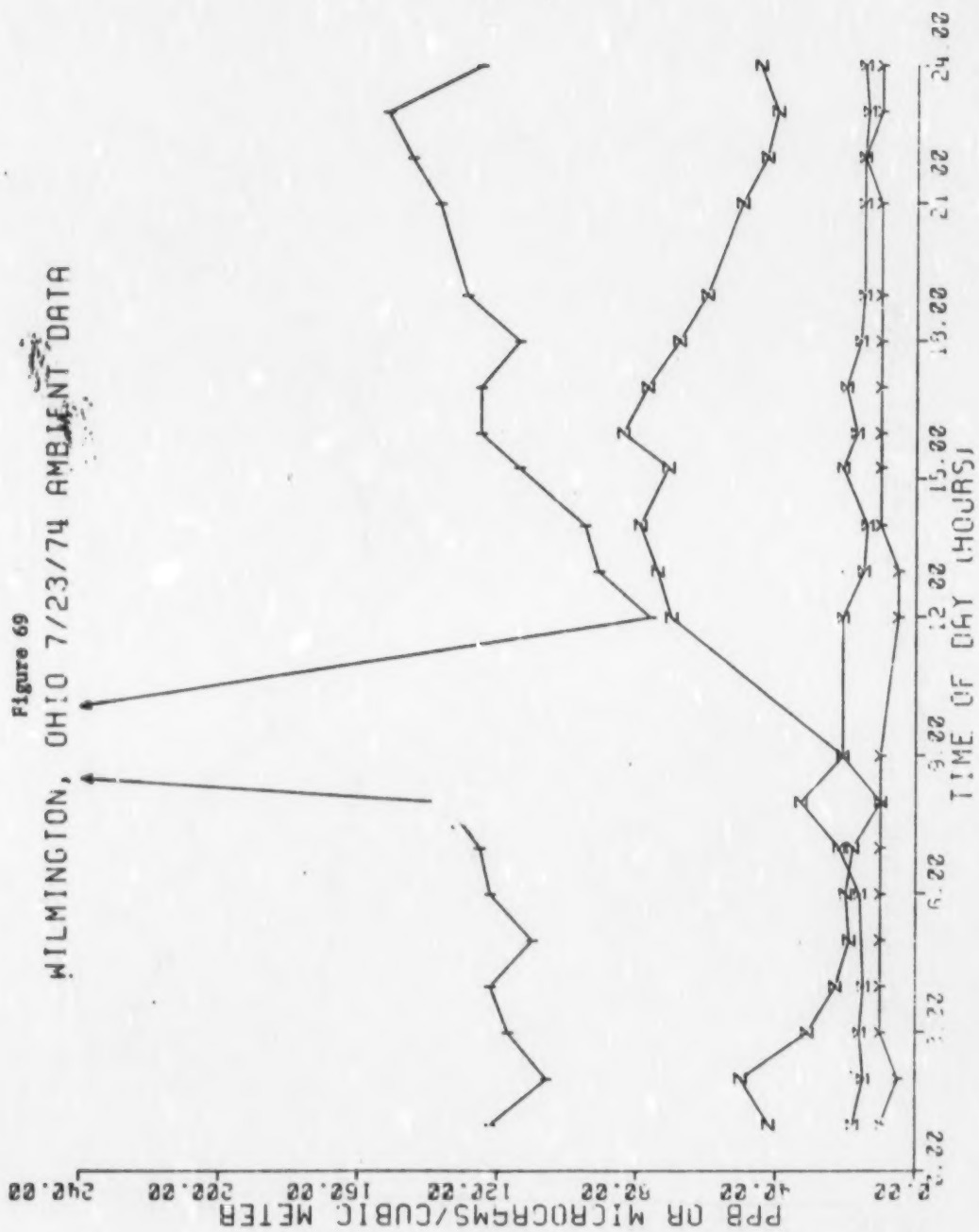


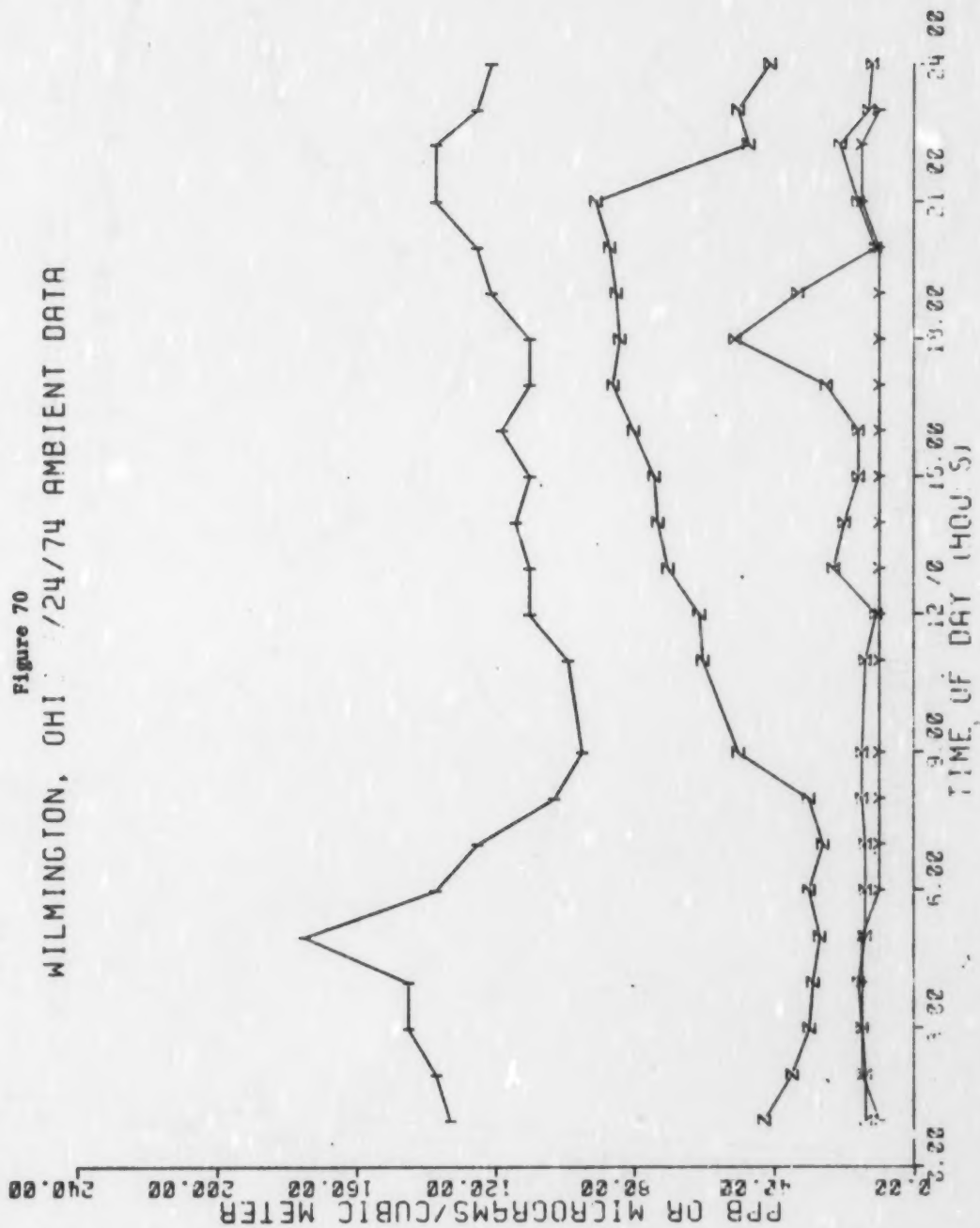
Figure 66
WILMINGTON, OHIO 7/19/74 AMBIENT DATA











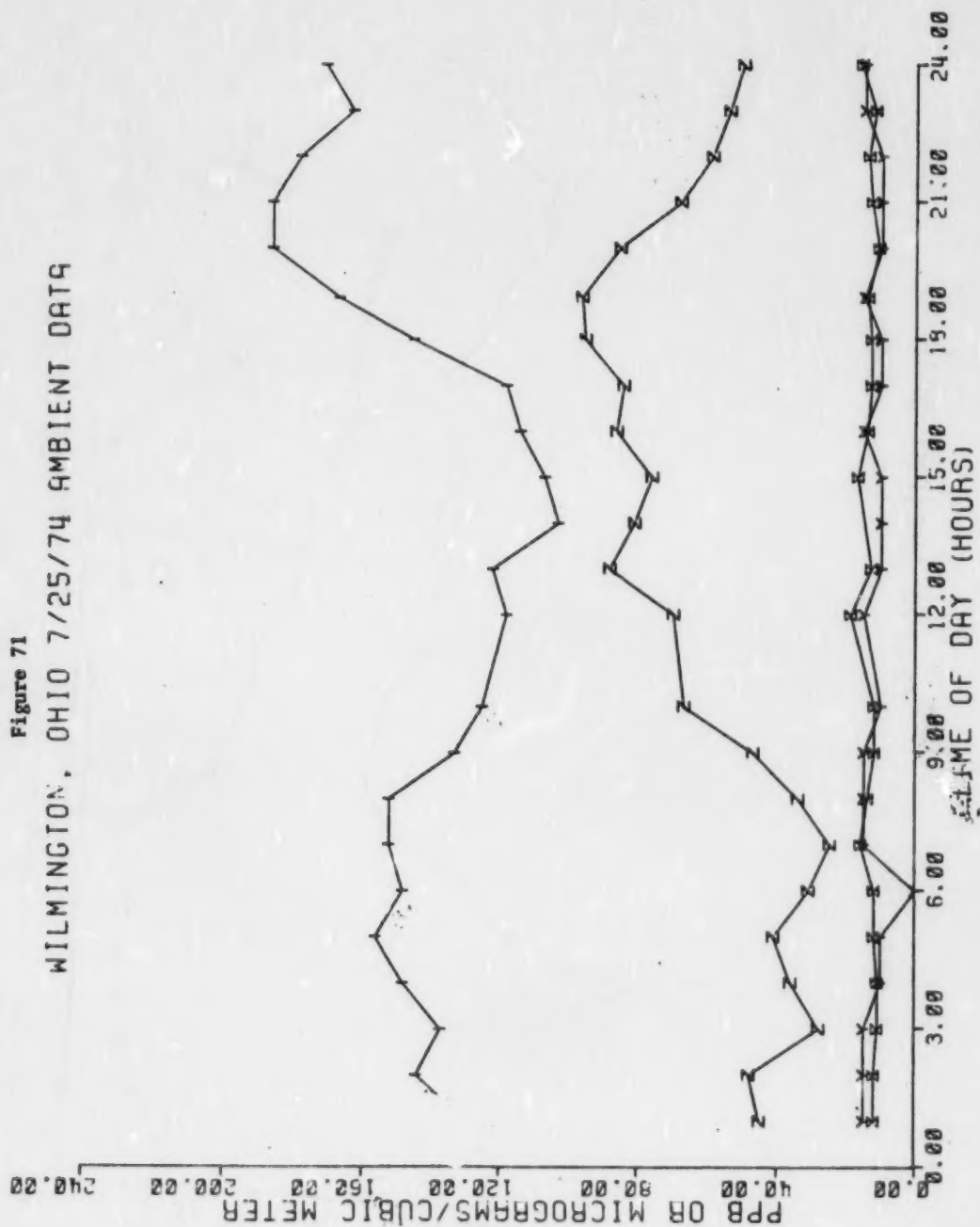


Figure 72
WILMINGTON, OHIO 7/26/74 AMBIENT DATA

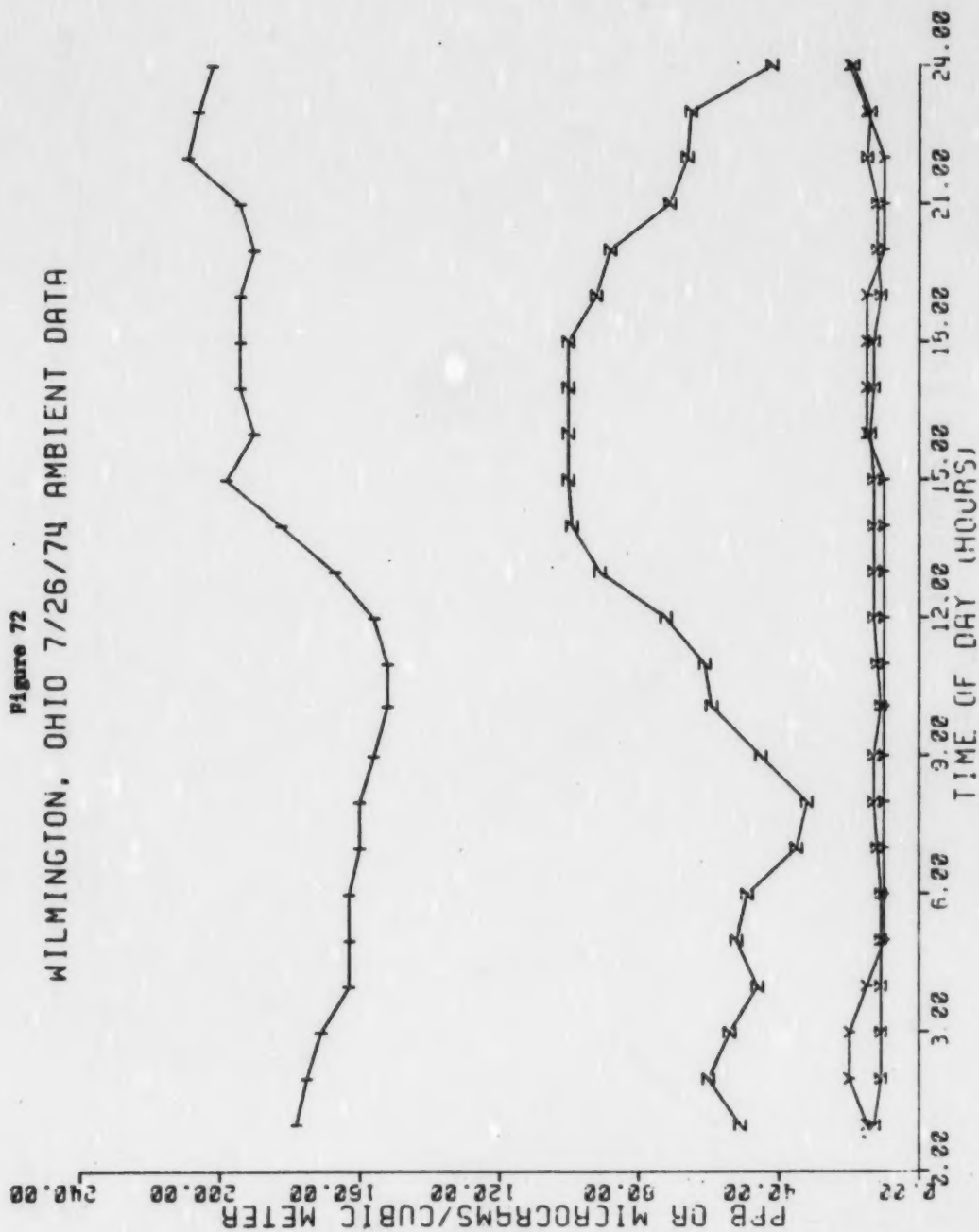


Figure 73
 WILMINGTON, OHIO: 7/27/74 AMBIENT DATA

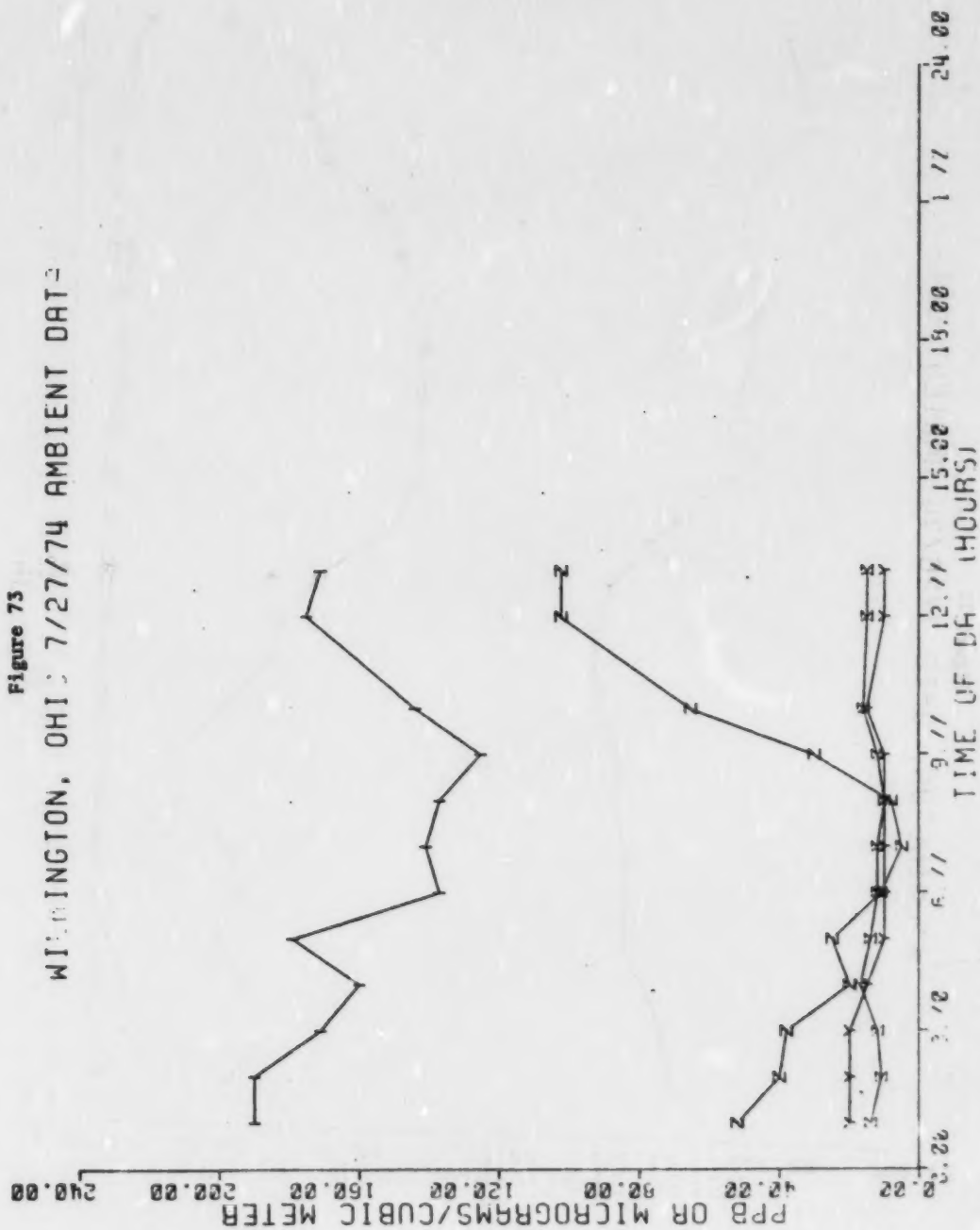


Figure 74
WHITEFACE MOUNTAIN 3/15/74 GRADIENT DATA

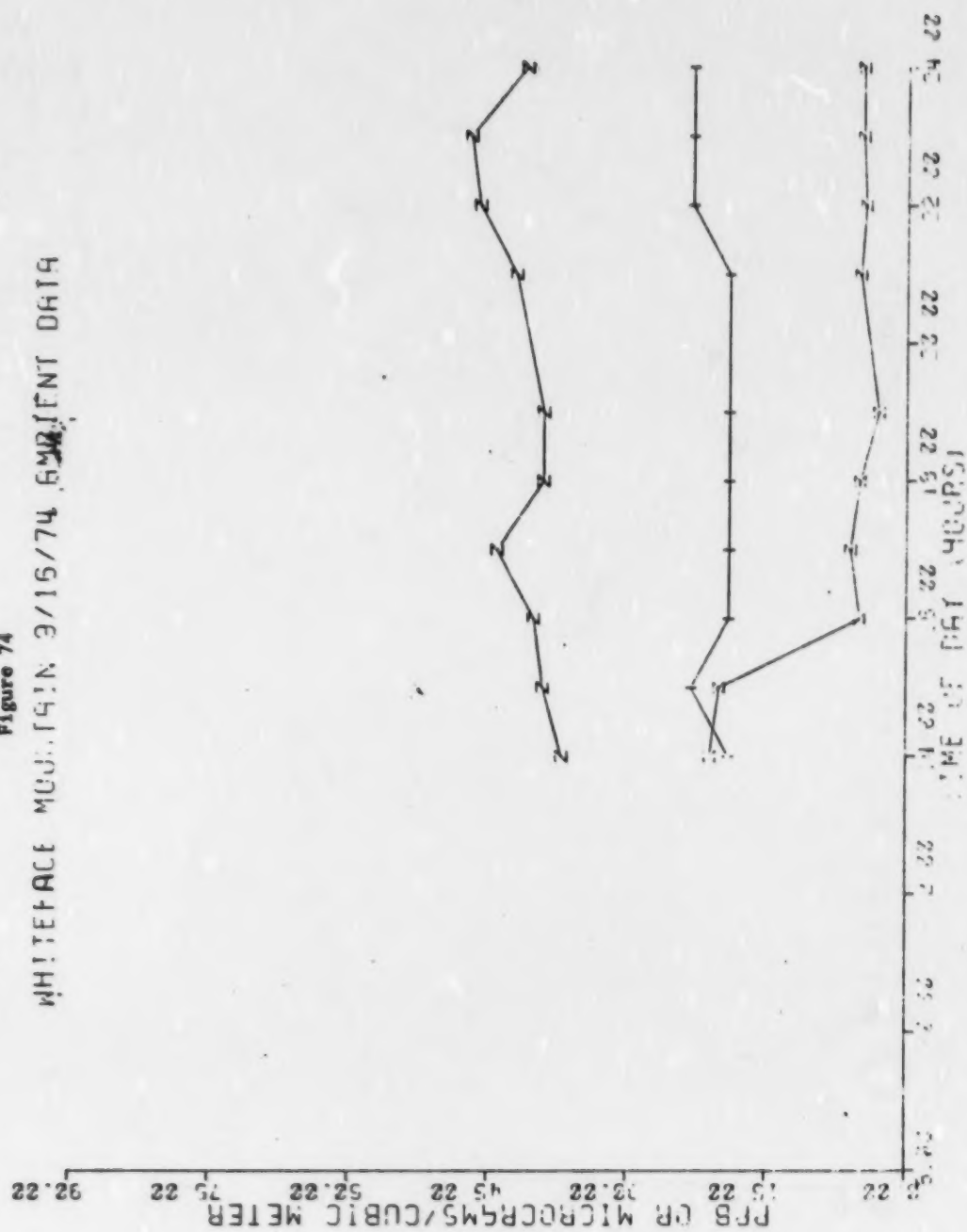


Figure 75
WHITEFACE MOUNTAIN 9/17/74 AMBIENT DATA

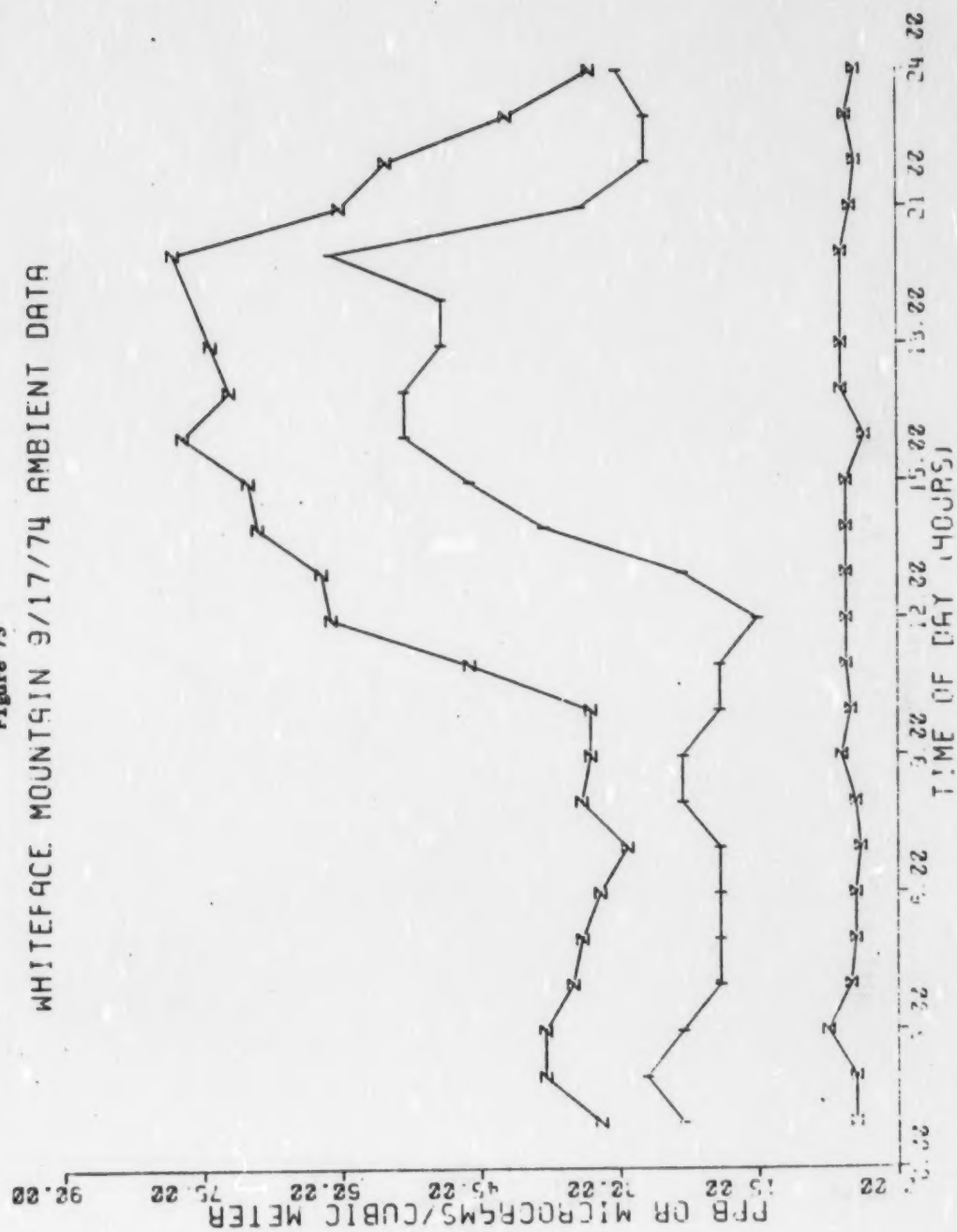


Figure 76
WHITEFACE MOUNTAIN 9/18/74 AMBIENT DATA

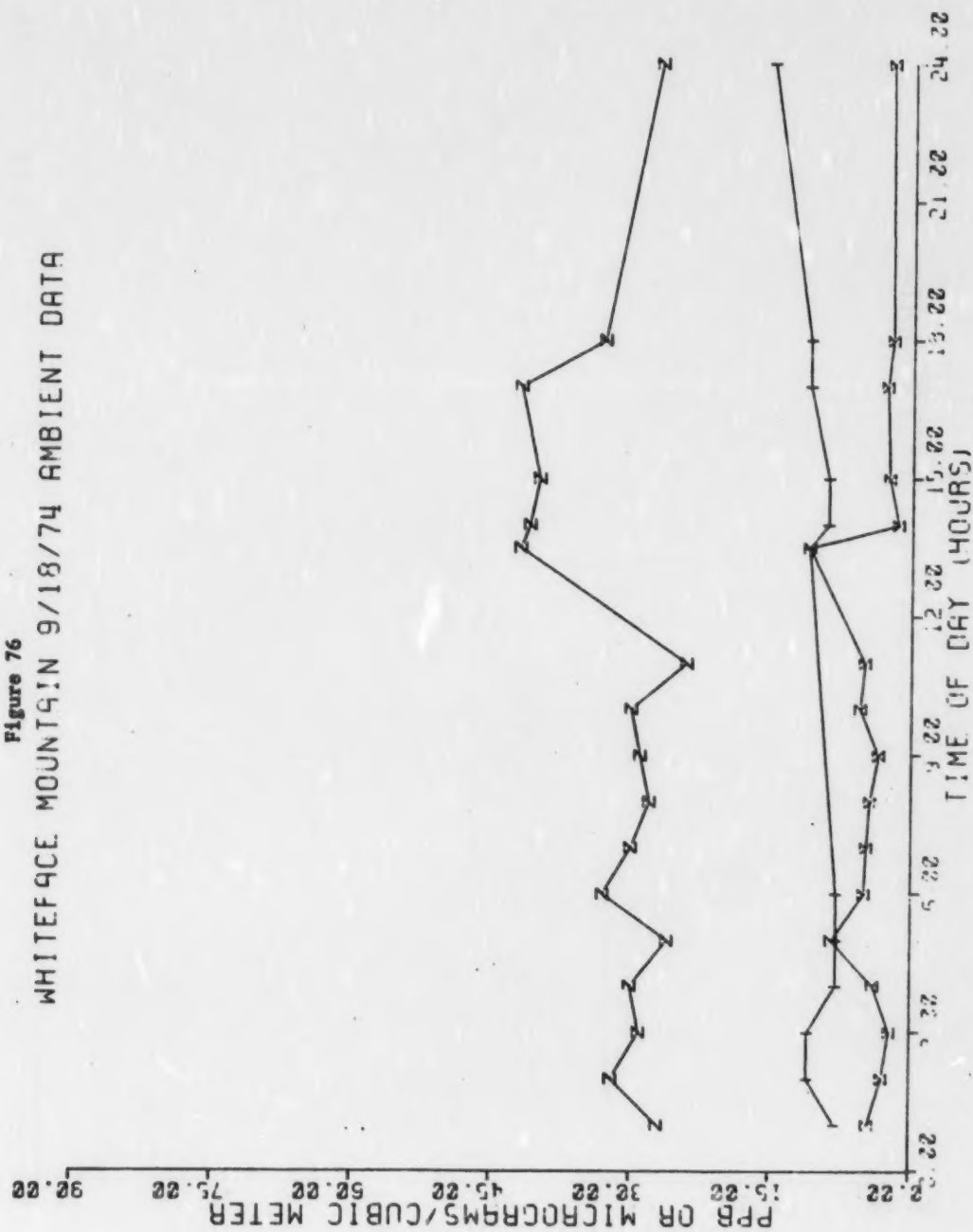
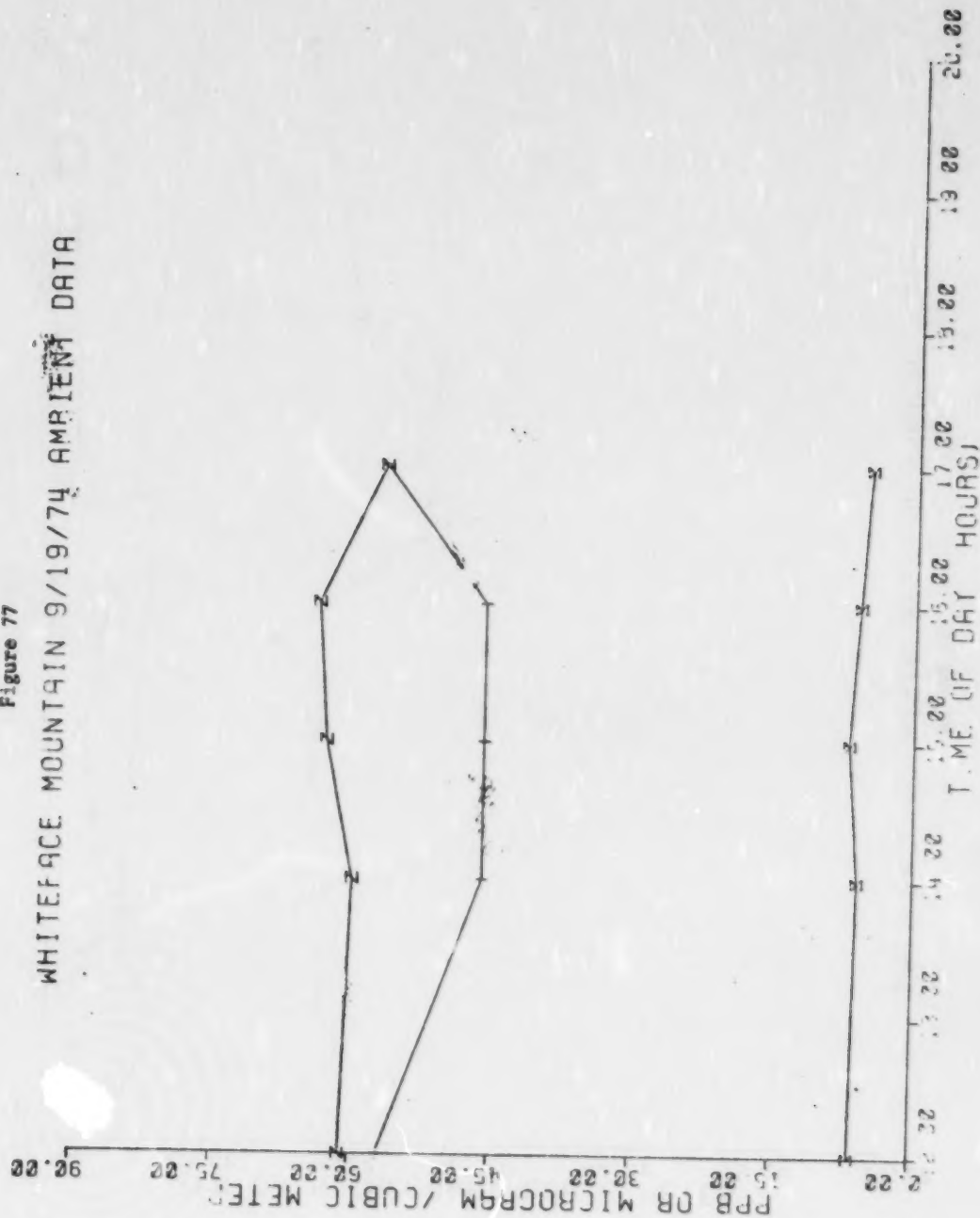
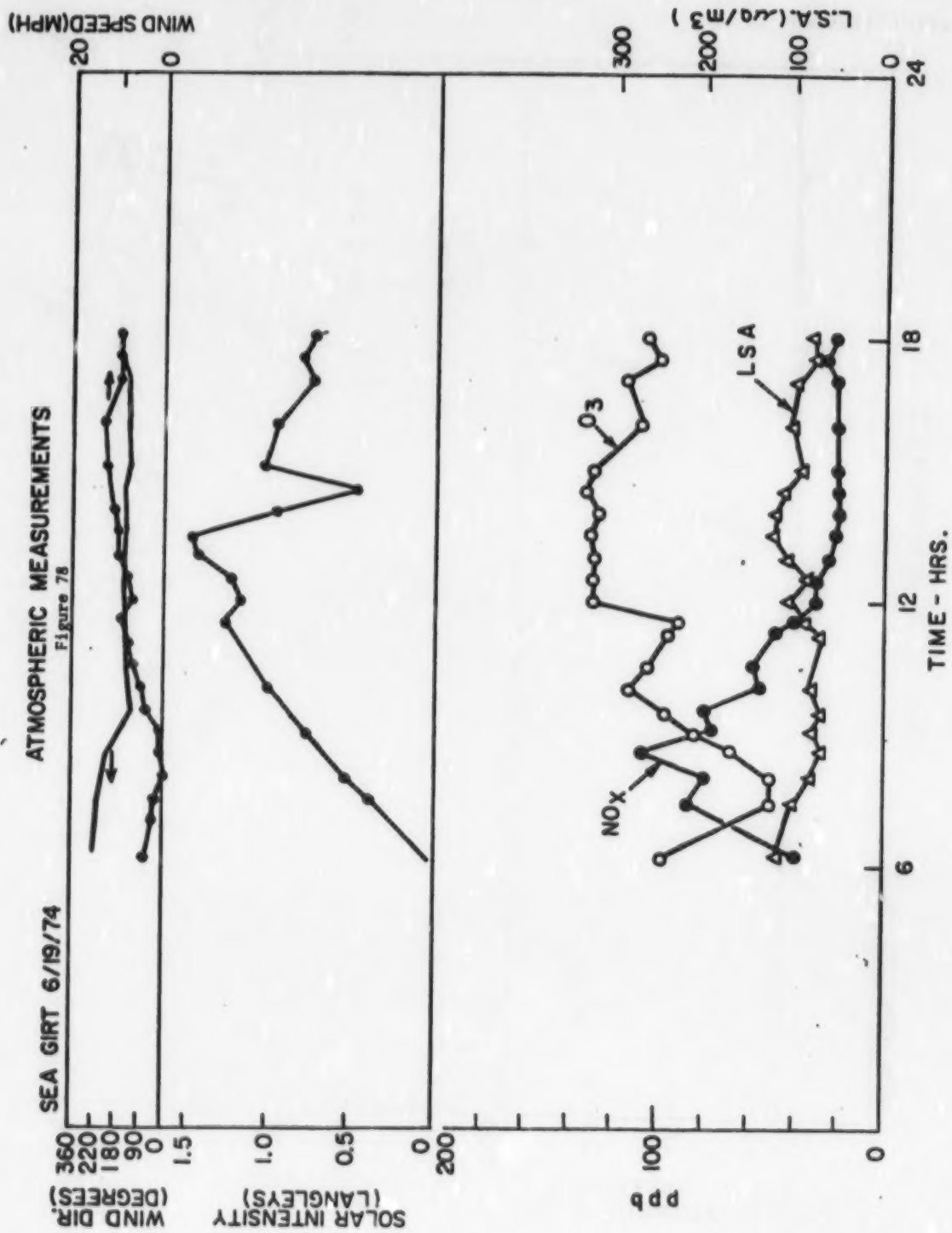
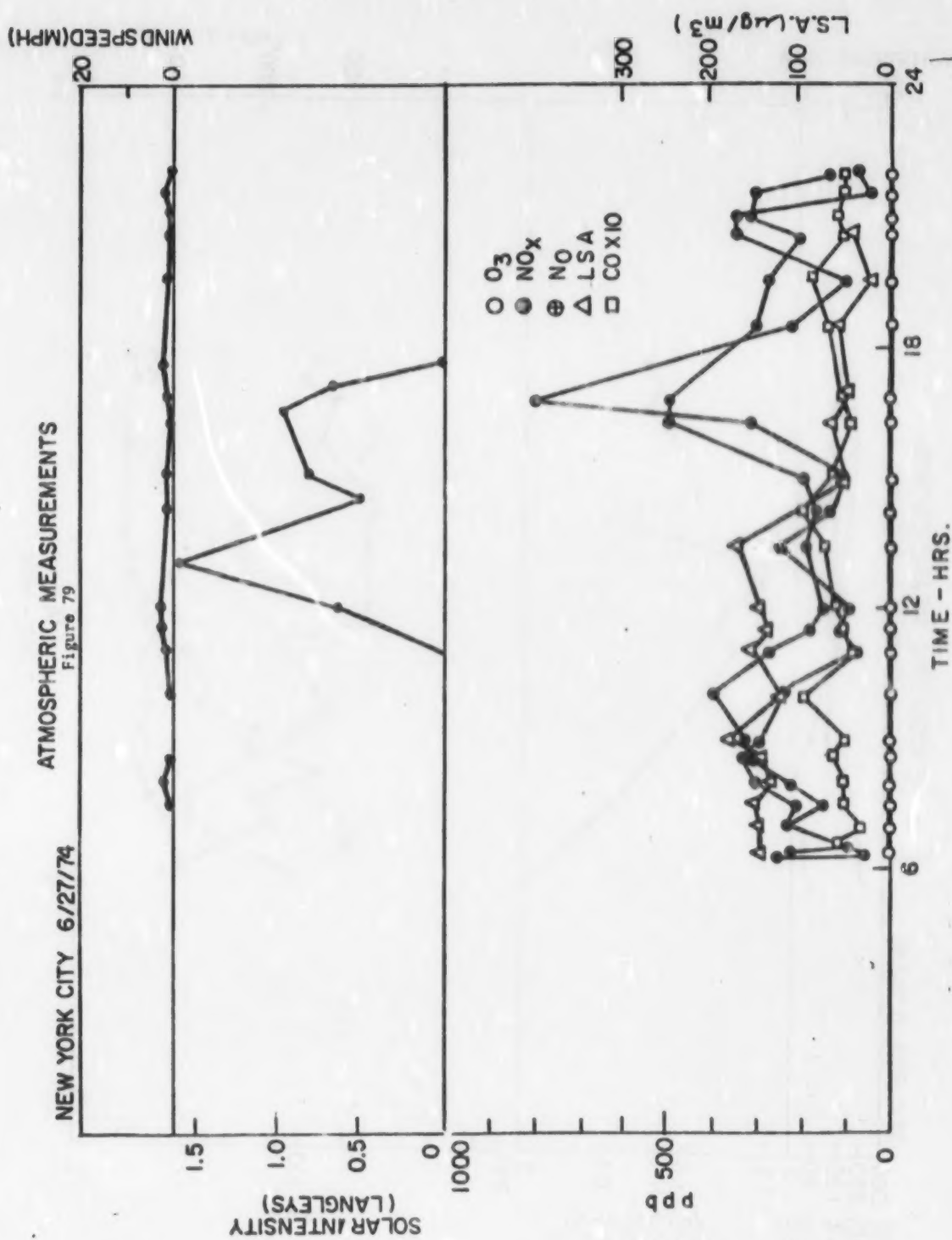
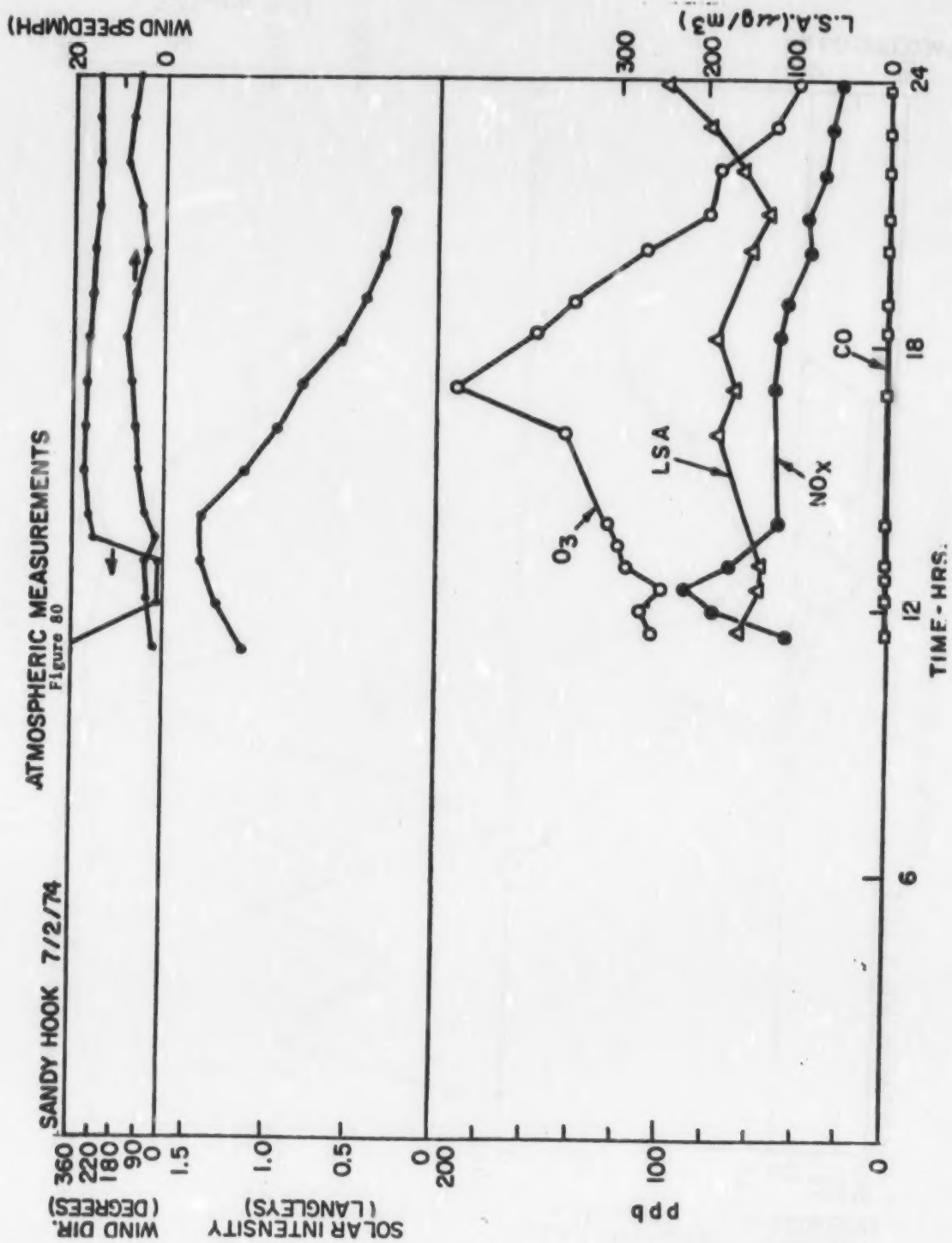


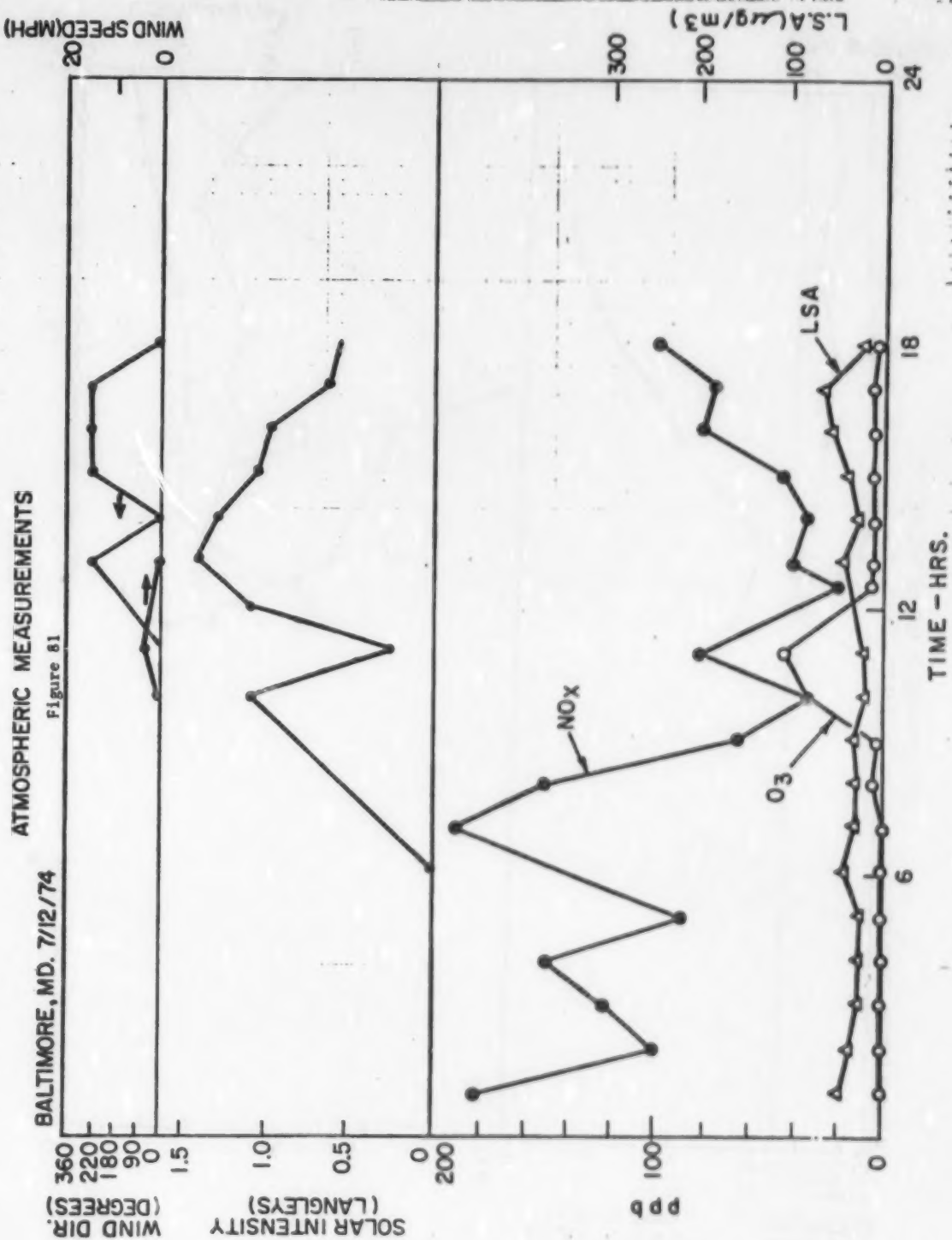
Figure 77
WHITEFACE MOUNTAIN 9/19/74 AMBIENT DATA











The maximum, minimum and average data of Table 13 for all the halogenated compounds are indicative of a complex variable emission pattern and a strong dependency on meteorological factors and should be representative of the lower and upper limits one can expect at typical urban and non-urban locations. However, the Bayonne, N.J. data show that, at times, meteorological conditions are probably more significant than local emission patterns. At this location not only were many of the maximum but also minimum halocarbon readings obtained. The frequency of minimum halocarbon data in Bayonne, N.J. was understandably quite low when compared to rural area data, for example the Whiteface Mountains. Representative levels of halocarbons that one can expect in urban and rural areas are given in Table 14. Also included in Table 14 are data indicating a dramatic increase in halocarbon concentration as one enters an inversion layer from aloft.

The apparent ubiquitous nature of CCl_3F , CCl_2F_2 , CH_3CCl_3 and CCl_4 , the probability of their near exclusive anthropogenic origin, their significant emissions, their low solubility in water, and theoretical chemical and biological inertness all suggested, early in our experiments, that these compounds would continue to accumulate in the troposphere and upon photolysis in the stratosphere play a significant role in stratospheric chemistry. However, there were insufficient data on CCl_3F and CCl_2F_2 and no data on CCl_4 and CH_3CCl_3 which rigorously precluded their reactions with typical reactive tropospheric species such as $\text{OH}^\cdot$, $\text{O}^\cdot$, $\text{RO}^\cdot$, etc. The tropospheric stability of these four compounds is unequivocally demonstrated in Figures 82 and 83. In these experiments k_1 for NO_2 photolysis was 0.39/min. Accordingly, in terms of total energy input, our laboratory irradiation times are equivalent to much longer tropospheric irradiation times. Similar experiments were conducted in which characteristic reactive hydrocarbons were also present. Again, with the exception of the small initial decay attributable to surface adsorption, these halocarbons were stable. Since NO_2 was replenished periodically (up to 50 pphm NO_2 every 24 hours) during the course of the irradiation, reactive tropospheric intermediates were continuously available for reaction with the halocarbons.

While atmospheric CCl_3F , CCl_2F_2 and CH_3CCl_3 are clearly anthropogenic, the occurrence of CCl_4 in the atmosphere can not be accounted for from direct production emission data^(10,4). No valid explanation for the CCl_4 budget is available to date. Promising research in this laboratory supports the possibility of considerable atmospheric CCl_4 formation by the photodecomposition of chloroalkenes in the troposphere⁽⁴⁾.

6.2.2 "Non-Ubiquitous" Halocarbons -

C_2Cl_4 was measured at concentrations exceeding 0.06 ppb at least 50% of the time at all locations. In a short-term monitoring effort in New York City, levels as high as 9.8 ppb were observed. Similarly, CHClCCl_2 was observed over 90% of the time at all urban locations (except Baltimore) at concentrations exceeding 0.05 ppb. A large clean oceanic air mass had moved in during the Baltimore monitoring, which probably accounts for

Figure 82
 HALOCARBON (IN AIR) + 50pphm NO₂ + 50% RH + hv
 IN A 72 LITER PYREX GLASS REACTOR

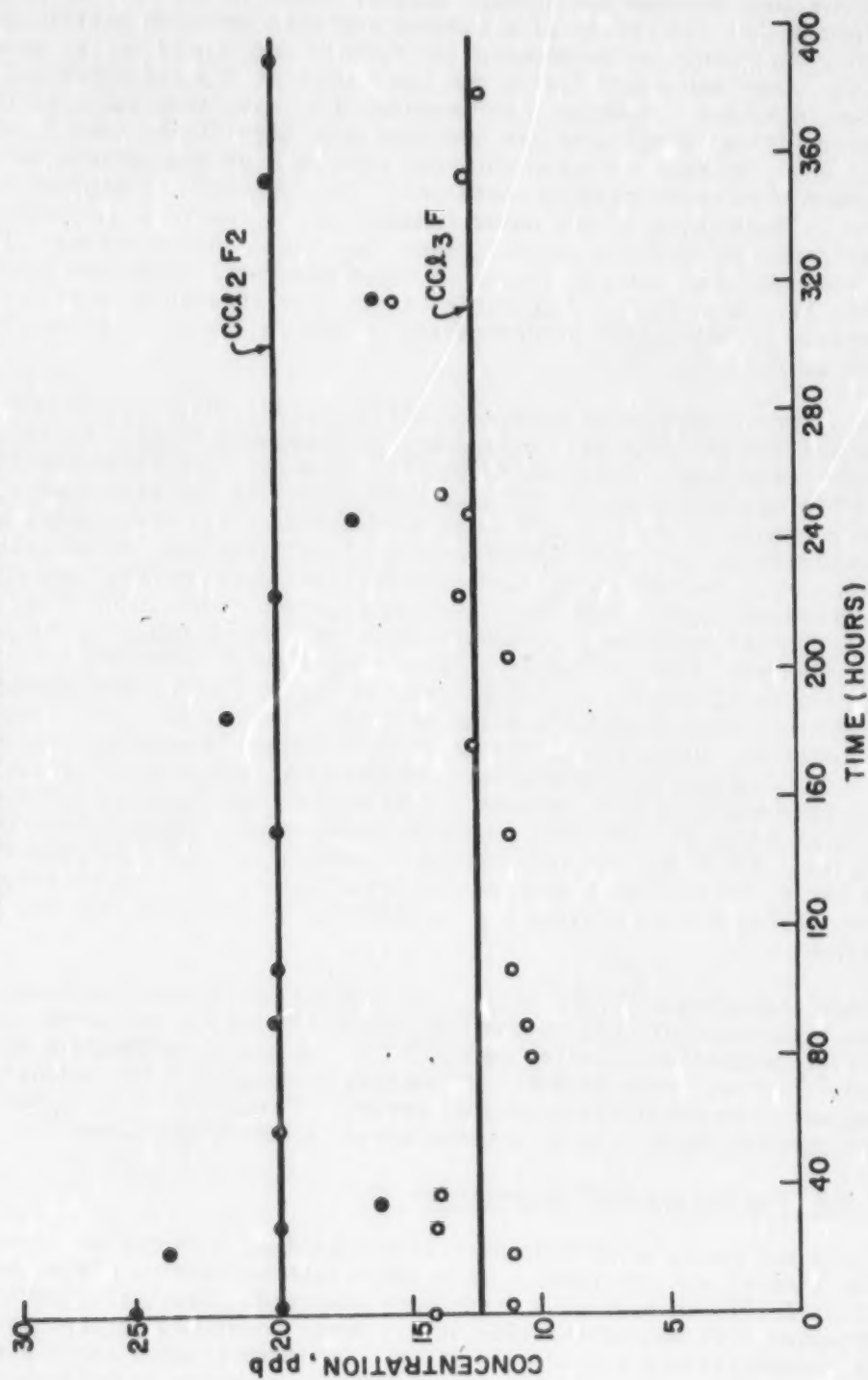
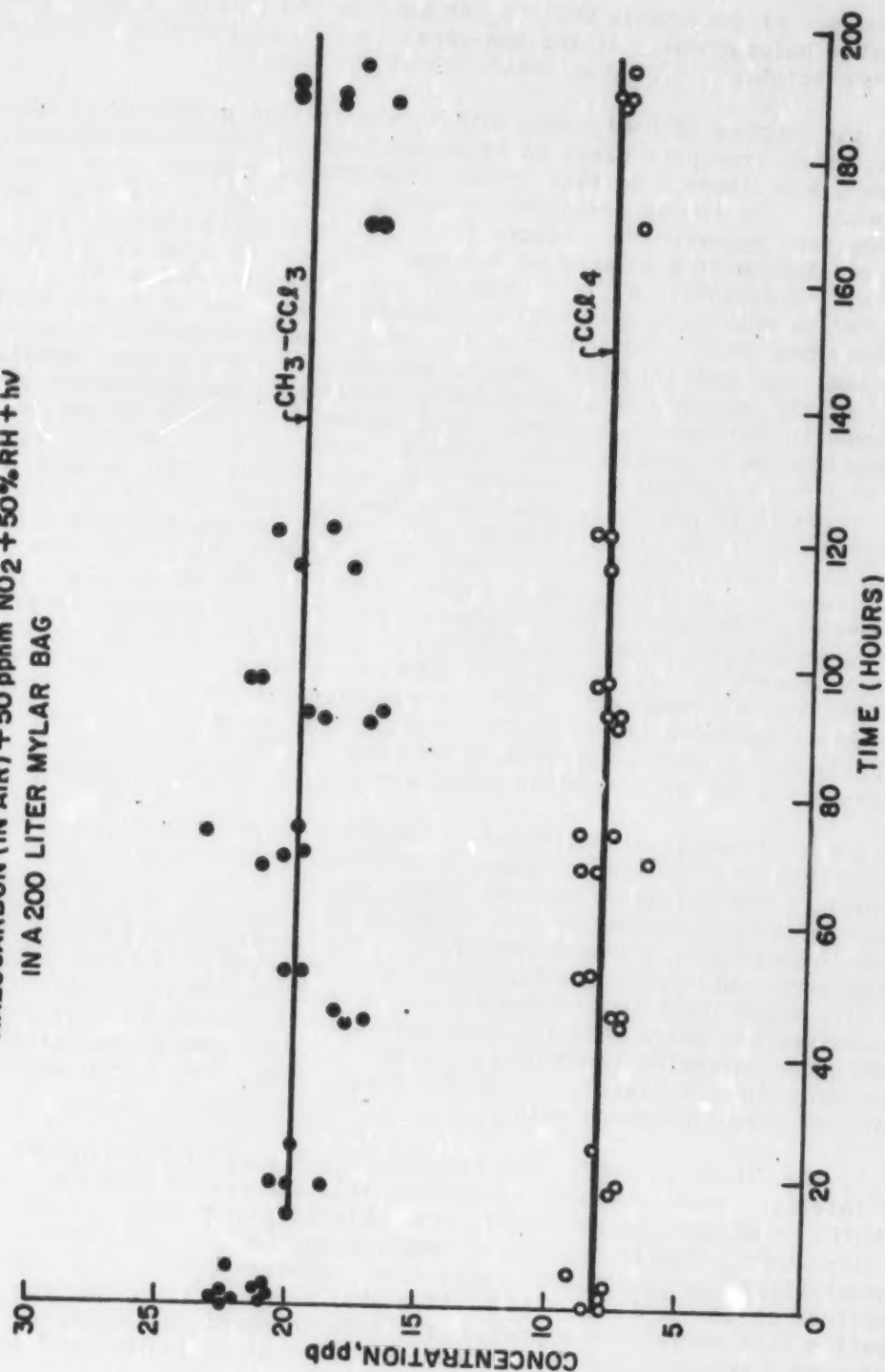


Figure 83

HALOCARBON (IN AIR) + 50 pphm NO₂ + 50% RH + hv
IN A 200 LITER MYLAR BAG



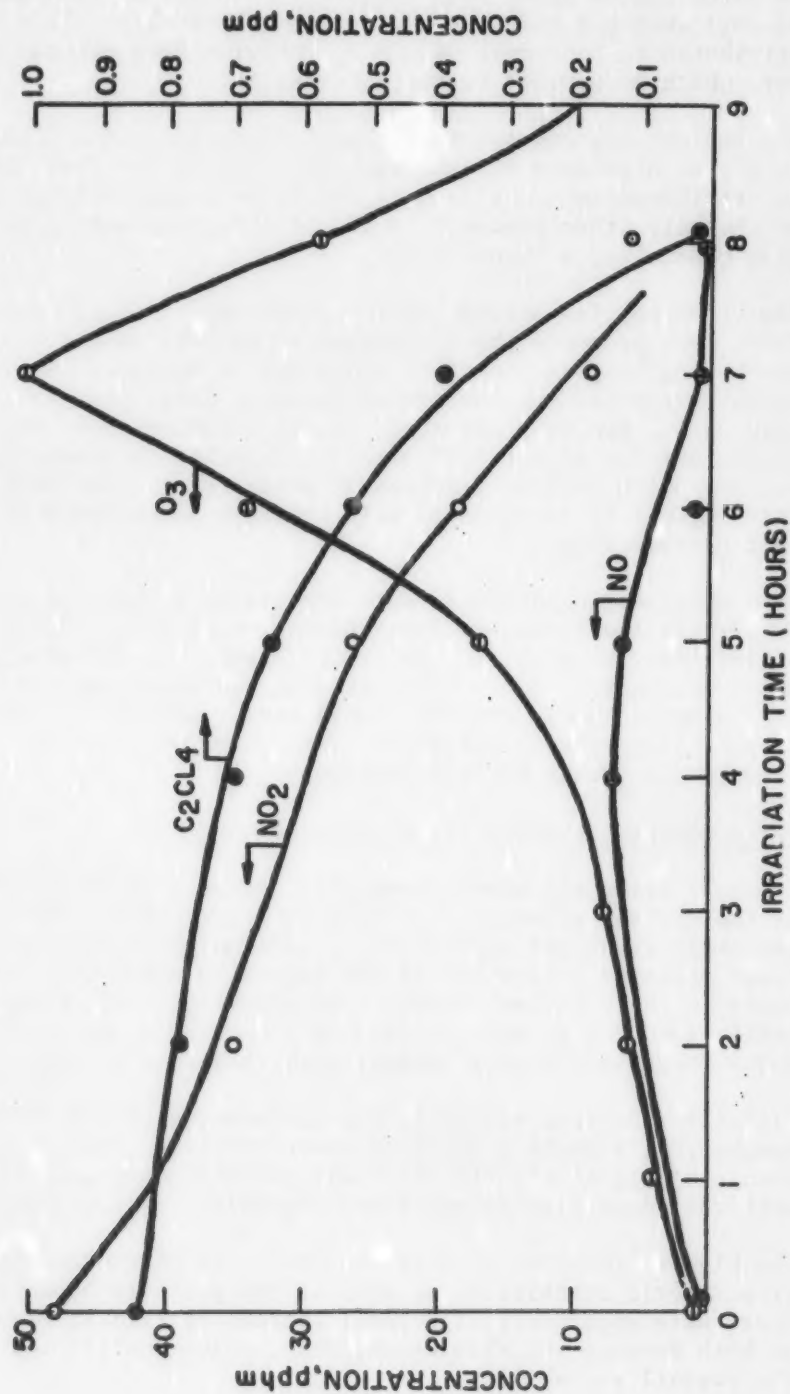
the absence of detectable CHClCCl_2 as well as the generally low levels of all other halocarbons. At the non-urban locations, however, this compound was undetectable (<0.05 ppb) about 70% of the time.

Since the sources of C_2Cl_4 and CHClCCl_2 are located primarily in urban areas, urban transport plays an important role in their distribution. However, superimposed on this is the tropospheric reactivity of these compounds. The tropospheric photochemical reactivity of CHClCCl_2 has already been reported⁽⁹⁾. Figure 84 is a concentration-time profile for the irradiation of a mixture of 0.8 ppm C_2Cl_4 and 50 pphm NO_2 in ultra-aero air (R.H.=50%). C_2Cl_4 is clearly quite reactive and would be expected to undergo significant photochemical degradation during transport to non-urban areas. Depending on the C_2Cl_4 source strength, meteorological dilution, sunlight intensity and the presence of other trace constituents, C_2Cl_4 or its predominant product COCl_2 accordingly may or may not be observed in the non-urban areas. As is clear from Figure 85 the percentage conversions on a chlorine basis of C_2Cl_4 to COCl_2 is about 60%. Recognizing the need for a sufficient reaction time, we calculate that an ambient concentration of 10 ppb C_2Cl_4 observed in New York City should lead to the formation of 12 ppb COCl_2 (TLV=100 ppb). Although quantitative data on the COCl_2 yield from CHClCCl_2 is not yet available, COCl_2 has been unequivocally confirmed to be a major product of the tropospheric photo-oxidation of CHClCCl_2 . The gas-phase phosgene-water reaction is probably insignificant as a removal mechanism for COCl_2 ⁽¹⁸⁷⁾, although particulate surface reactions and reactions of COCl_2 with other trace constituents, say NH_3 , may be important. This clearly suggests the need for a program of ambient measurements of COCl_2 . The rapid ozone decay in Figure 85 is probably due to a chlorine atom ozone chain reaction similar to the one proposed for the stratospheric ozone destruction by fluorocarbons⁽¹⁾.

The lower frequency of detection of CHClCCl_2 is probably due to a smaller source strength⁽¹⁸⁸⁾ and a higher tropospheric reactivity⁽²¹⁾. Additionally, however, urban transport may not always manifest itself in increased ground level halocarbon concentrations in non-urban areas due to the trapping of urban halocarbons in inversions aloft. The inversion data of Table 14 illustrates this point clearly. All halocarbon concentrations measured at this rural location at ground level were typically low. Halocarbon concentrations above 5000 ft. were similarly characteristically low. Within the inversion layer however (1500 ft), halocarbon concentrations were many factors higher, say 35 for CCl_3F , than their corresponding ground level or above inversion values.

CH_3I , SF_6 , CH_2CHCl , CHCl_3 , and $\text{CCl}_2\text{F}-\text{CClF}_2$, the other halogenated compounds of interest, were generally measurable less frequently than C_2Cl_4 and CHClCCl_2 and, for the most part, traceable to nearby sources. The noteworthy characteristic feature of tropospheric CH_3I is its general non-detectability at locations remote from the ocean (Table 14). Indeed, Lovelock et al.⁽¹⁰⁾ found a 100 fold higher mean surface ocean concentration than aerial concentration for this compound and suggested the ocean as a source. The lack of detectability at sites remote from the

Figure 84
 $\text{C}_2\text{Cl}_4(\text{IN AIR}) + 50 \text{ ppm NO}_2 + 50\% \text{ RH} + h\nu$
 IN A 200 LITER TEFLON BAG
 $(k_1 = 0.39/\text{MIN})$
 MAX PHOSGENE = 0.95 ppm



ocean is likely due to tropospheric reactivity (Figure 85). It should be noted that a ghost peak frequently appears at the same retention time as CH_3I when one uses a glass syringe repeatedly. This is tentatively attributed to heterogeneous CH_3I synthesis from unknown ambient precursors which accumulate on the glass walls.

The ambient SF_6 concentrations were typically below 0.001 ppb although levels as high as 0.005 ppb were observed in New York City. The latter is attributed to leaks from SF_6 -dielectric high-voltage transformers, or the only other probable source of this compound, a nearby meteorologist conducting a tracer study.

The reported link between Angiosarcoma and vinyl chloride monomer (pending TLV=1 ppm) prompted the inclusions of CH_2CHCl in the halocarbon ambient monitoring program. CH_2CHCl could not be measured at all locations (sensitivity >10 ppb) except at Delaware City, Delaware, where levels as high as 1.5 ppm were observed. These readings were obtained downwind from a complex of chemical plants. Experiments conducted in this laboratory which will be reported in detail at a later date demonstrate that CH_2CHCl is tropospherically reactive and hence will not accumulate in the troposphere.

Both CHCl_3 and $\text{CCl}_2\text{F}-\text{CClF}_2$ were detectable at most urban locations at a relatively low frequency (sensitivity >0.01 ppb). $\text{CCl}_2\text{F}-\text{CClF}_2$ exhibits significant tropospheric stability (Figure 86) and should accumulate in the troposphere. Since CHCl_3 absorbs radiation only well below the 290 nm tropospheric cut-off (CHCl_3 $\lambda_{\text{max}} = 175$ nm) it can only undergo thermal tropospheric reactions. Its structure however, suggests minimal tropospheric decay by such reactions.

6.2.3 Ambient Variability of Halocarbons -

Table 17 lists the eleven compounds measured in order of the "variability" of the ambient values, as defined in section 6.1. This quantity, though extremely crude and statistically indefensible, nevertheless gives a rough relative indication of the degree to which these compounds fluctuate in their ambient levels. Interestingly, the compounds fall rather neatly into two groups - a "low variability" group with values of 50-70% and a "high variability" group, with values of 95-130%.

With the exception of C_2Cl_4 , all the members of the first group are tropospherically stable, which no doubt explains their relatively constant values. CCl_4 is clearly the least variable compound, which is consistent with the ideas already expressed regarding its possible sources.

The high variability of CH_3I and C_2HCl_3 is understandable in view of their tropospheric reactivity, as well as the probable oceanic source of CH_3I . There were apparently high local sources of F_{113} at Bayonne, and of CHCl_3 at both Bayonne and Wilmington, Ohio, which contributed considerably to the overall variability.

Figure 85
 CH_3I (10 ppb in air) + 50 ppm NO_2 + 50% RH + $h\nu$
 IN A 200 LITER TEFLON BAG
 ($k_1 = 0.39/\text{MIN}$)

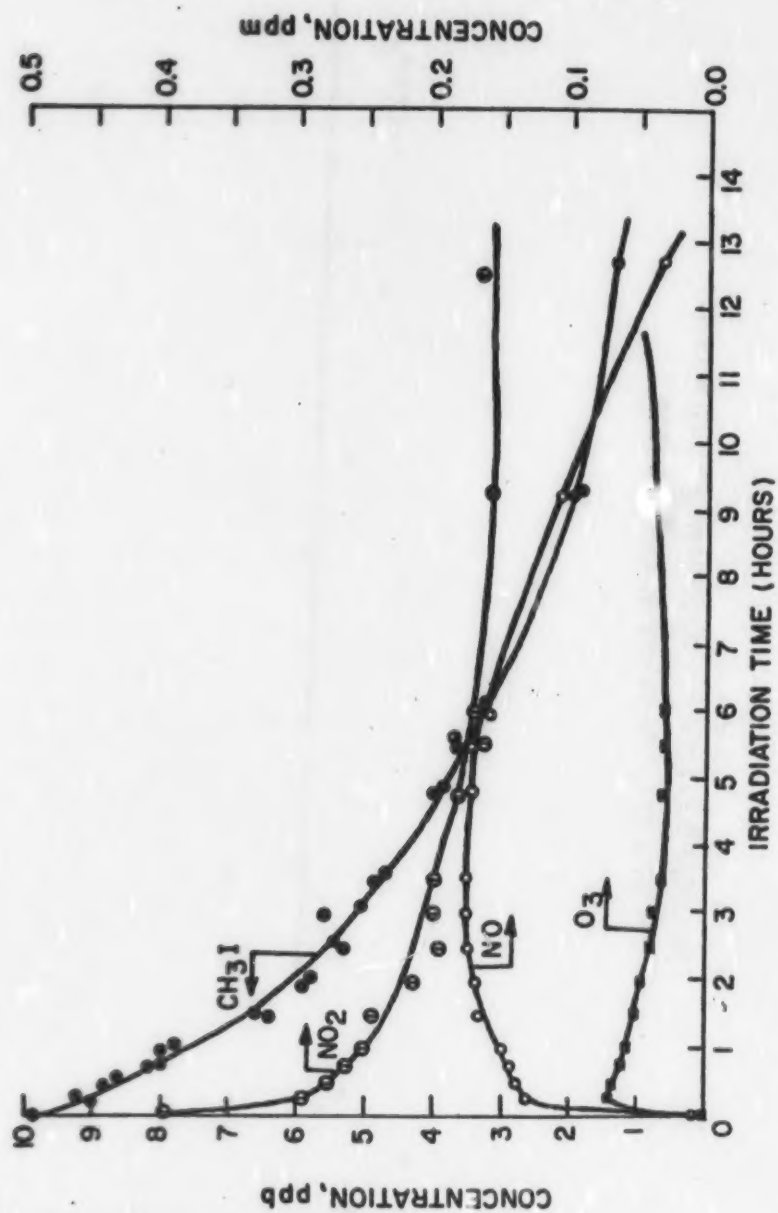
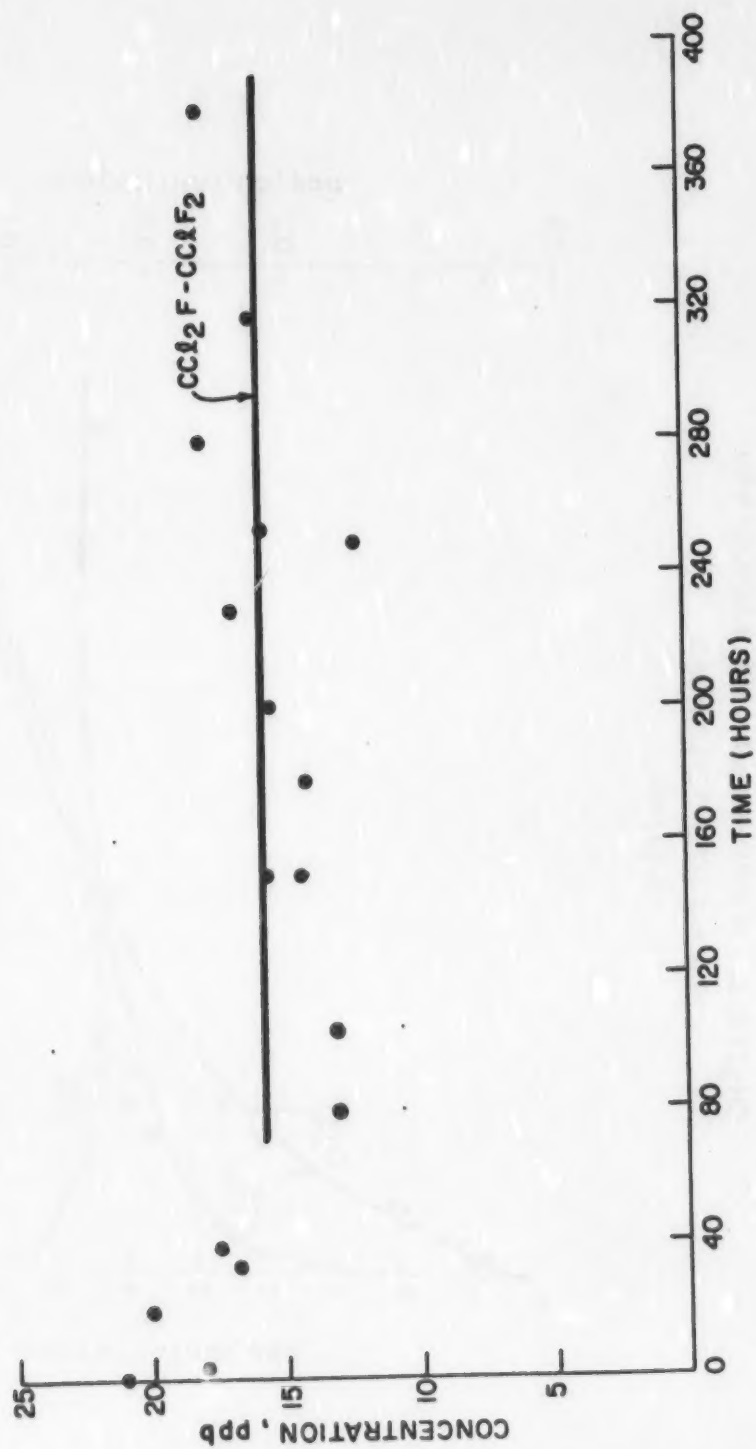


Figure 86:
 HALOCARBON (IN AIR) + 50 ppm NO₂ + 50% RH + hν
 IN A 72 LITER PYREX GLASS REACTOR



6.2.4 Ambient Halocarbons as Tracer for Large Air Masses -

Because of their characteristic spatial and temporal distributions, wide gradation of atmospheric reactivity, and amenability to ultra-trace analysis, halocarbons are potentially useful for elucidating complex atmospheric transport phenomena. Figure 87 is a diurnal concentration-time profile for O₃, light scattering aerosol (LSA) and several halocarbons obtained at Whiteface Mountains, New York, a relatively clean air site (LSA 20 to 60 µg/M³). Ozone concentrations are seen to increase gradually from 0800 to 2000 hours. The net increase of 20 ppb from 1100 hours to about 1600 hours can be attributed to either tropospheric synthesis and/or transport. However, the ozone concentrations increasing until 2000 hours to a maximum of about 65 ppb can not be accounted for by synthesis. Since the halocarbons generally originate in urban areas their concomitant increase with ozone and particulates is an unequivocal proof of urban transport. Stratospheric injection of ozone can be discounted since this would be associated with deep vertical mixing and hence, in the absence of significant simultaneous transport, a decrease in halocarbon levels. Stratospheric injection occurring simultaneously with transport can be discounted since CCl₄ would have to decrease, because of its known decreasing vertical concentrations profile (16) combined with its uniform distribution in urban and non-urban locations. This is clearly demonstrated in Figure 88 where the levels of CCl₄ in New York City and the Whiteface Mountains are remarkably similar. The corresponding data for the other halocarbons shows their expected much higher urban levels.

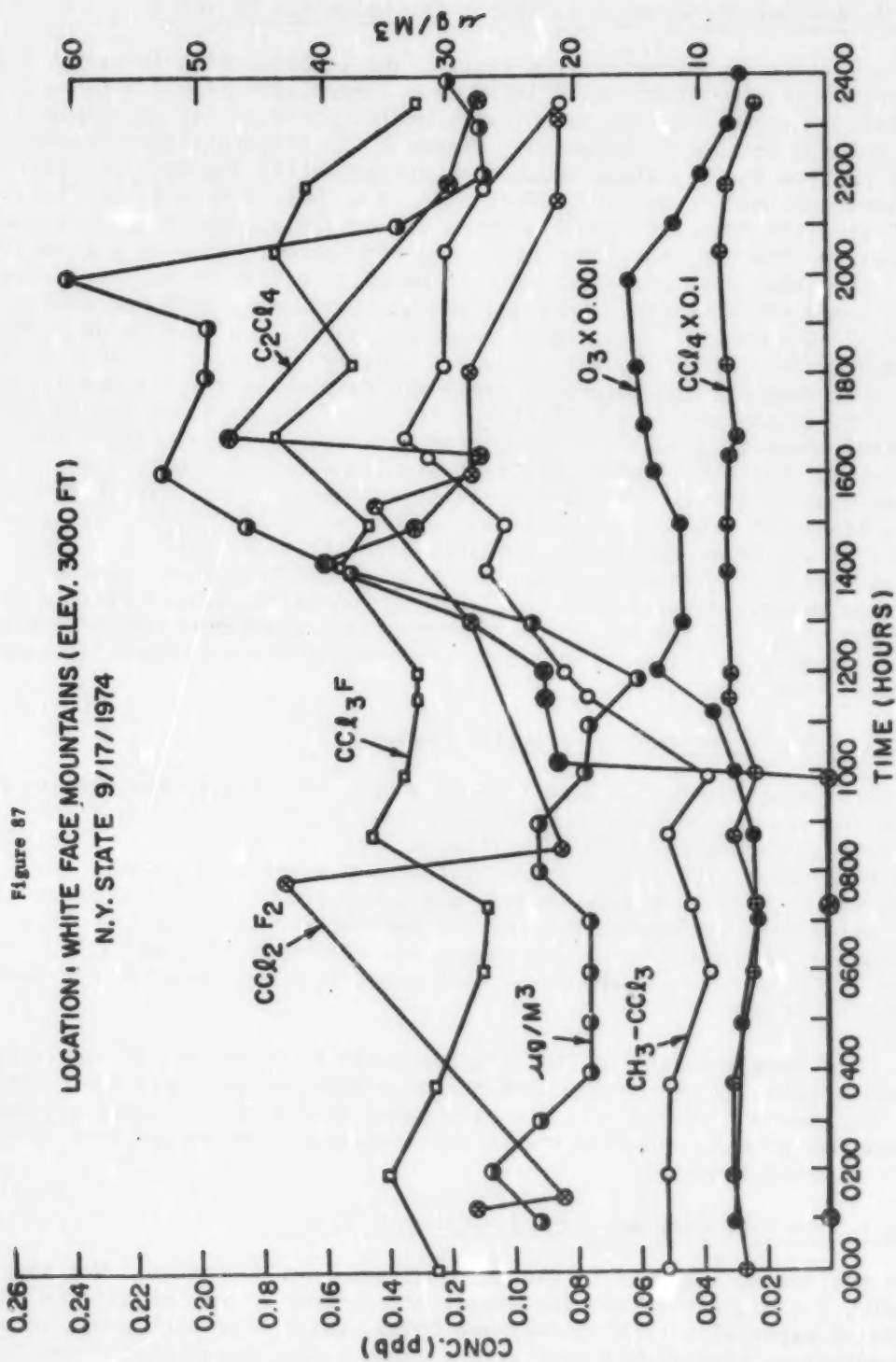
6.2.5 Seagirt monitoring - General comments -

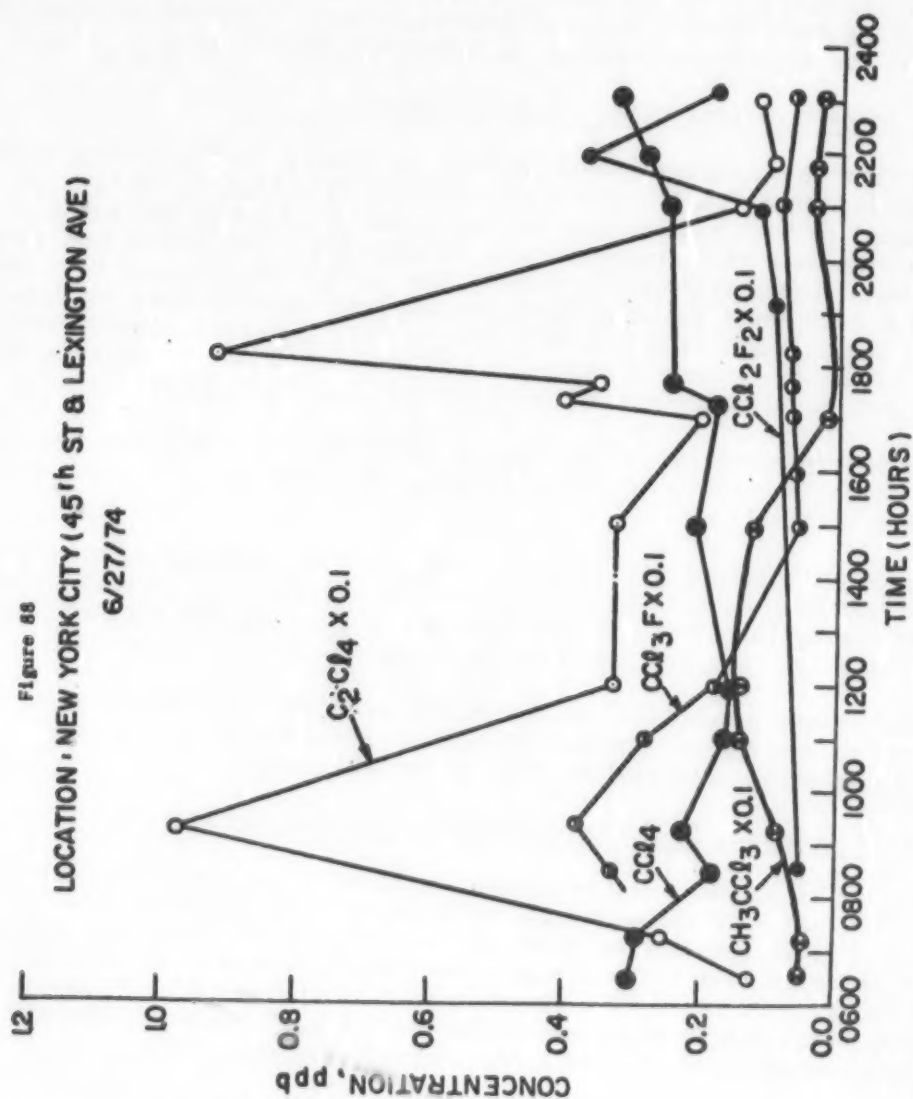
At this location breezes were typically from the land in the morning and from the sea in the afternoon. The pattern of NO_x and O₃ levels on 6/19/74 is consistent with this (Figure 78). In the absence of destructive agents the ozone levels will remain through the night, an observation made by others in some non-urban areas. With the onset of the afternoon sea-breeze, all the fluorocarbon levels dropped. This is especially noticeable with the ubiquitous compounds F-11 and 111T. The drop in CCl₄ is less pronounced, consistent with its relative non-dependence on location.

The data here demonstrate that caution needs to be exercised regarding samples taken by the ocean, with on-shore breezes, as being representative of background. At Seagirt, the halocarbon levels were clearly substantially above background, concurrent with the seabreeze. In other words, polluted air is being recycled.

6.2.6 New York City monitoring - General comments -

The monitoring site was in the heart of mid-town Manhattan. Not unexpectedly, the highest values for almost all compounds were registered here. This is especially true of F-11 and C₂Cl₄, which were each about an order of magnitude higher here than at any other site. Local wind speed and





direction are largely meaningless because of the proximity of tall buildings - however the general wind direction over the city during the monitoring period was northeast.

Extreme fluctuations in all the measured parameters are apparent, again no doubt due to the peculiarities of the monitoring site. It is possible, however, to discern the increases in nitrogen oxides during the morning and evening rush hours. On 6/27/73 there is even a peaking to coincide with the evening theatre traffic in this area (Figure 79).

6.6.7 Sandy Hook monitoring - General comments -

On all four days, exceptionally high maximum ozone levels were observed (180 to 200 ppb). On the first day (7/2/74) this high O_3 can be attributed to high hydrocarbon and NO_x emissions from inland being transported over the monitoring site (Figure 80). The halocarbon levels, which were characteristically higher than background, support this view. At about 1300 hours the wind direction changed suddenly from north to west. The air mass from the west was probably more contaminated with ozone precursors, since there was a simultaneous dramatic increase in C_2Cl_4 and, to a lesser extent, some of the other halocarbons.

NO was characteristically very low, which further supports the concept of O_3 formation upwind of the monitoring site, and is consistent with the high O_3 levels.

The monitoring period was just prior to a holiday weekend, with high traffic density on the New Jersey Turnpike and other major roads, west of the monitoring site. CO levels were seen to increase concurrently with oxides of nitrogen, as would be expected.

Because of the possibility of analytical artefacts in the converter of the NO_x detector, care should be taken in considering the NO_2 data. The NO_2 values could well include PAN, as is well known.

6.2.8 Wilmington, Delaware monitoring - General comments -

As far as halocarbons are concerned, this was a fairly "clean" site, with F-11 and F-12 values as low as anywhere. Except for somewhat higher CH_3I values (due no doubt to proximity of the ocean), measurable vinyl chloride, which has already been commented upon and lower CCl_4 , this location is not unlike the Whiteface Mountain site. O_3 levels were, however, exceedingly high, exceeding the 0.8 ppm standard. The air was clearly contaminated, but in a "non-urban" fashion.

6.2.9 Baltimore, Maryland monitoring - General comments -

As stated earlier, a large clean air mass arrived from the ocean during the monitoring period. The air was thus much cleaner than should normally be expected in an urban location such as this. The very high NO_x levels

(Figure 81) are almost certainly due to the proximity of local sources. The site was only a few hundred yards from the tunnel entrance of Interstate 95, which was vented by large fans. Also close was a D.O.T. maintenance building having very heavy truck traffic throughout the day. The lack of wind during the night would permit oxides of nitrogen from these local sources to remain in the vicinity.

6.2.10 Wilmington, Ohio monitoring - General comments -

Based on halocarbon levels, the air at this site was considered to be mildly polluted. Surprisingly, CH_3I was detectable on a few occasions, despite its high tropospheric reactivity and the remoteness of the site from the ocean. A local source is possible, such as the one which apparently existed for CHCl_3 . (CHCl_3 had the highest average value here of any site, and the highest variability.)

The typical diurnal trend of O_3 levels can be seen at this location, but the absence of a diurnal pattern of NO and the high O_3 concentrations even in the evening, is indicative of transport.

A considerable amount of additional data was accumulated during this monitoring period, as part of a collaborative effort with EPA. For example, halocarbon levels were measured in aircraft samples taken above and below an inversion line. A wide variation between the levels was noted - for example, F-11 was 0.3 ppb above the inversion layer (6000 ft.) and 8 ppb below it (4500 ft.). All this data has been supplied separately to the EPA and will no doubt be incorporated in due course into a full report on this monitoring effort.

6.2.11 Whiteface Mountain monitoring - General comments -

The evidence for large-scale urban transport to this location has already been discussed (Section 6.2.4). Otherwise the site is the cleanest of those studied, and the minimum halocarbon levels are probably typical of background. As stated earlier, agreement with background values reported by others is quite good.

6.2.12 Bayonne, New Jersey monitoring - General comments -

This was the first site at which regular halocarbon analyses were carried out. Up till May, 1973 only F-11, F-12, CCl_4 and CH_3I were measured, but after August 1973 the analytical procedures had been developed sufficiently to permit measurement of F113, CHCl_3 , 111T, TCE and PCE. The data here were taken over a larger period and less frequently than at the other sites, so it was not considered worthwhile to compute daily averages, as has been done in Table 15 for the other locations. Monthly averages are given instead.

This site showed perhaps the greatest variability of halocarbon levels. The highest values of all compounds measured except TCE (where NYC had a slightly higher value) were recorded here, as well as the lowest values of F-11, CCl_4 ,

TCE, CH₃I, CHCl₃ and F113. The site is distinctly urban, but appropriate meteorological conditions can evidently provide typical background levels, on occasion.

SECTION VII

PHOTOCHEMICAL REACTIVITY STUDIES

The compounds discussed in the following subsections (7.1 to 7.10) were each subject to simulated tropospheric sunlight under a variety of conditions. Those which showed no evidence of significant decay under tropospheric conditions were further examined for their behavior under simulated stratospheric sunlight conditions. The experimental details have been described in Section 4.

7.1 F-11, F-12 and F113

7.1.1 Results -

In all systems simulating tropospheric irradiation neither Freon-11, Freon-12 nor Freon 113 reacted. Preliminary investigations had indicated that these compounds would not react; as a result the following experiments were pursued: Freon-11 and Freon-12 were irradiated in ultra zero air at 50% relative humidity in Mylar bags for a period of 13000 minutes. The system investigated contained Freon-11 and Freon-12 and NO₂. The nitrogen dioxide concentration was monitored daily during the course of this experiment and was replenished in an effort to maintain a concentration of 50 pphm NO₂. Freon-11 and Freon-12 concentrations were also monitored daily. The same system was investigated in a glass reactor, and identical experimental procedures were followed. In both systems, there was no net decomposition of either compound (indicated by no decrease in concentration) as shown in Figure 82. A similar result was obtained with F-113 (Figure 86). The aforementioned experimental scheme was repeated with approximately 1 ppm hydrocarbon "A" in the system, and the results obtained substantiated the previous findings (Figure 89). Freon-11 was next introduced into the 72 liter Pyrex glass reactor. The investigated mixture was composed of Freon-11, ultra-zero air at 50% relative humidity and nitrogen dioxide. Nitrogen dioxide was replenished daily to maintain 50 pphm, and Freon-11 concentration was monitored as a function of irradiation time (almost 400 hours). The result of this experiment (Figure 90) indicated no net decrease in the concentration of F-11 indicating no photoreactivity of these compounds in a polluted environment. A similar result was obtained with F-12.

Figure 91 shows the effect of simulated stratospheric photolysis on F-11 and F-113. In these experiments the halocarbons in ppb binary mixture with zero air were irradiated in the 1-liter quartz reactor by the 450 watt high-pressure mercury vapor lamp.

7.1.2 Discussion -

The results presented above conclusively establish that these compounds do not react chemically in a polluted environment under the influence of tropospheric sunlight. Their chemical inertness, and the fact that these

Figure 89
**CFCL₃ PLUS NO₂ AND HYDROCARBON
 IRRADIATED IN ULTRA ZERO AIR IN A MYLAR
 REACTION CHAMBER**

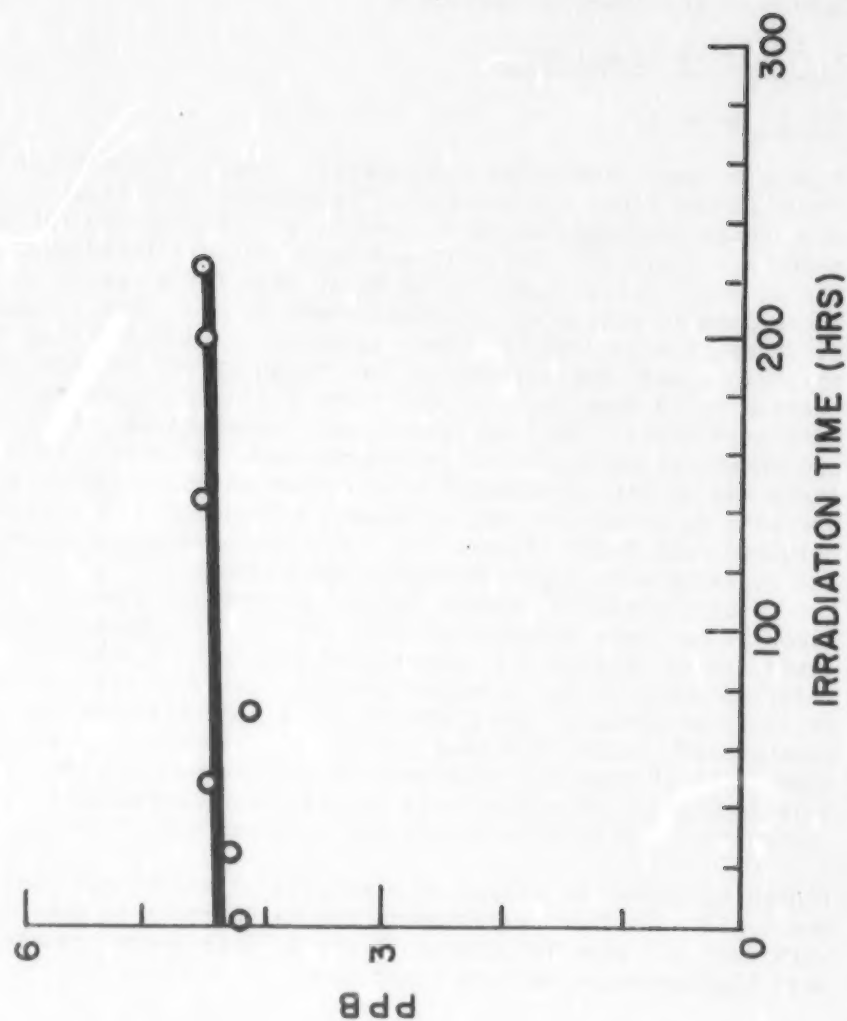


Figure 90
 FREON-11 (CCl_3F) FREON-12 (CF_2Cl_2) PLUS NITROGEN
 DIOXIDE IRRADIATED IN ULTRA ZERO AIR IN A 72 LITER
 PYREX GLASS REACTOR, REPLENISHING NO_2

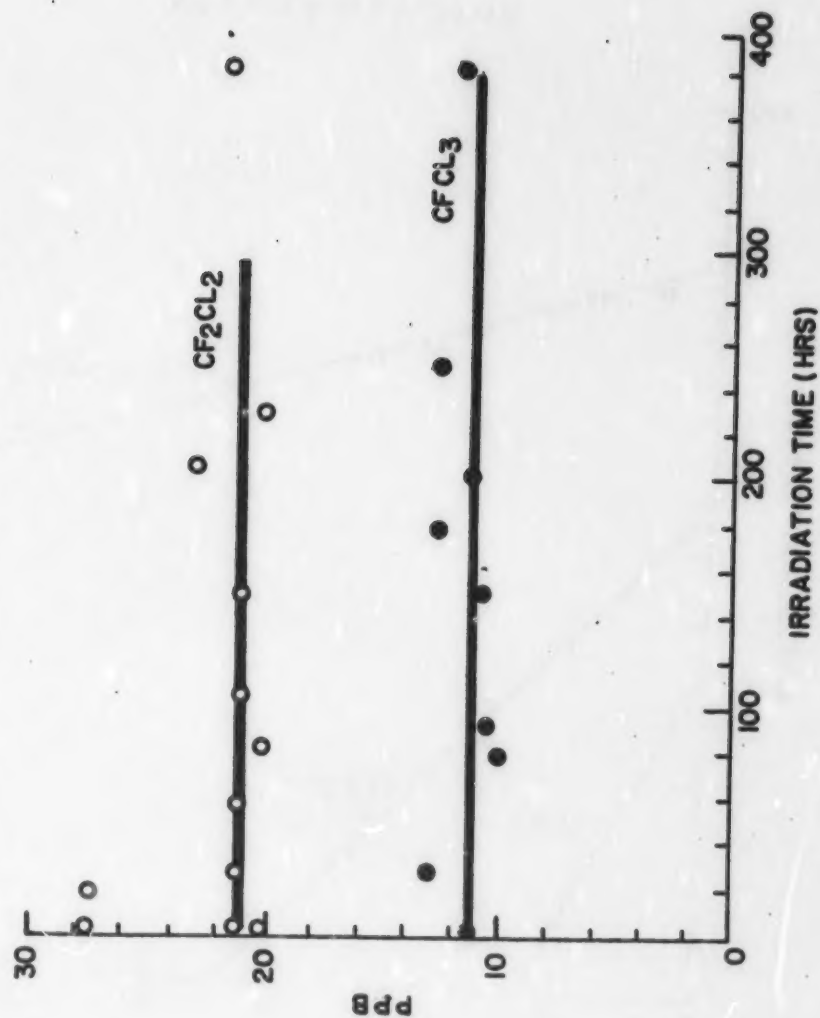
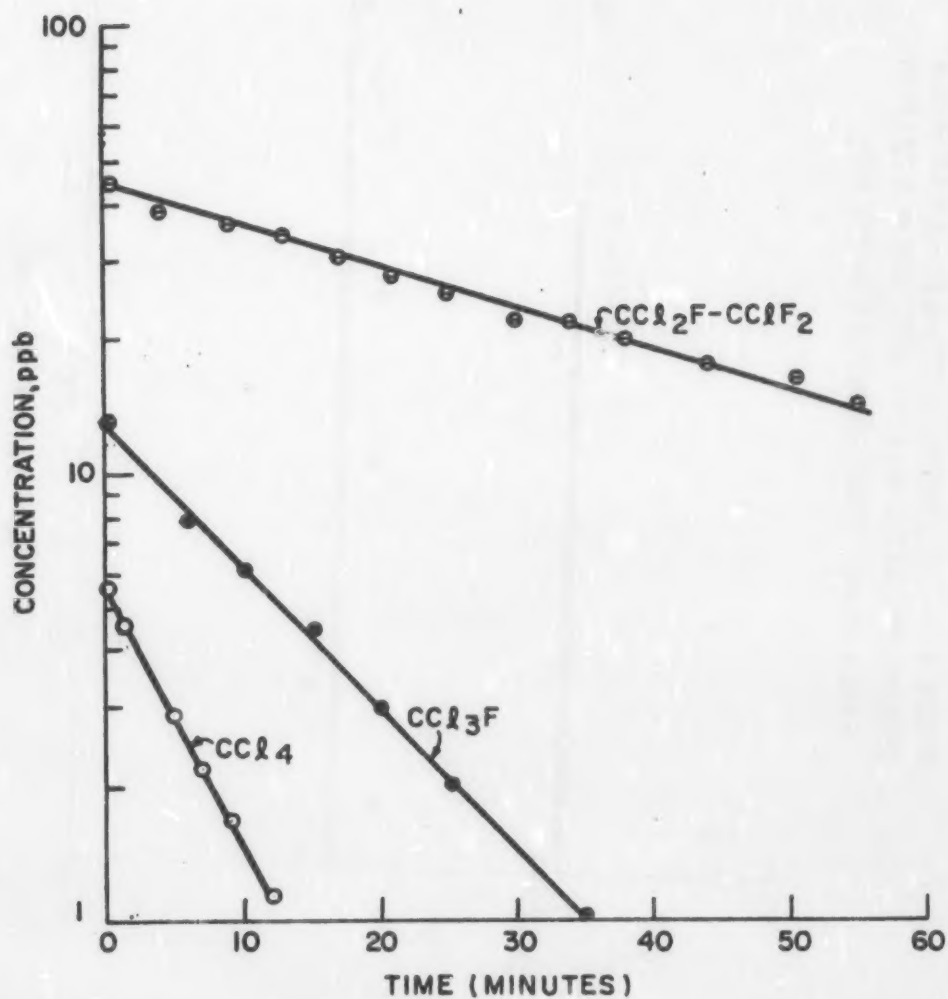


Figure 91
HALOCARBON DECAY IN A 1 LITER
U.V. (>2200Å) REACTOR
HALOCARBON + AIR + U.V.



compounds are transparent to wave lengths longer than $2900\text{\AA}$ ⁽¹⁸⁹⁾ serve to substantiate our findings that photolysis of these compounds does not occur in the troposphere. Molina et al.⁽¹⁾ have proposed stratospheric photolytic dissociation of F-11 and F-12 to CFCl_2 and Cl , and to $\cdot\text{CF}_2\text{Cl}$ + $\cdot\text{Cl}$, each reaction creating two odd electron species, a Cl atom and a free radical. The ultimate proposed sink involves a catalytic chain reaction leading to a net destruction of ozone and atomic oxygen as follows:

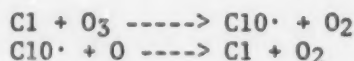


Figure 91 clearly establishes the stratosphere as a sink for these compounds. From the slopes and a consideration of the average light intensity of 0.34 watts/cm^2 used in our experiments - a level some 400 times the solar irradiance at the top of the stratosphere⁽⁴²⁾, the respective half-lives of CCl_3F and $\text{CCl}_2\text{F}-\text{CClF}_2$ of 10 and 31.5 minutes correspond to minimum stratospheric half-lives in hours of 69 and 217 hours.

With the expectation of 10-30 fold increase in concentration of freons in the atmosphere, based on the assumption that present fluorocarbon production and emission would continue, Molina and Rowland⁽¹⁾ calculated atmospheric lifetimes in the range 40-150 years. Stratospheric photodissociation of freons, it was proposed, would produce significant amounts of chlorine atoms, and lead to destruction of atmospheric ozone by the chain process above. In fact it was suggested⁽¹⁹⁰⁾ that these compounds in the stratosphere have already caused a 1% to 2% reduction in stratospheric ozone concentration, enough to cause an estimated 10,000 new cases of skin cancer each year in the U.S. Reduction in the level of ozone which heats the stratospheric air as it absorbs radiation could also cause changes in global air circulation patterns and subsequent climatic changes at the earth's surface. The overall effects on man are difficult to evaluate at this time. There could possibly be damage to the eyes, sunburn and aging of the skin.

It has, however, been pointed out⁽¹⁹¹⁾ that ozone concentrations less than 10% at atmospheric pressure and room temperature, the photosensitized decomposition of O_3 by chlorine is not a chain reaction, but has a quantum yield of only 2. Further, the radicals can react not only with O_3 but also with other atmospheric constituents such as H_2O and NO_2 to form, for example, HClO_3 , HClO_4 and HNO_3 . Such competitive processes would, of course spare the ozone from the full effects of the chlorine atoms produced by u.v. photolysis of freons.

7.2 Perchloroethylene

7.2.1 Results -

In all irradiated systems investigated perchloroethylene reacted to 95% completion. However, the rate of reaction was substantially different in each system investigated. Hydrocarbons exerted an inhibiting effect

on the reaction rates.

Perchloroethylene in Ultra Zero Air at 50% R.H. - In the photolysis of perchloroethylene in ultra zero air at 50% relative humidity the compound was 100% reacted in 1.5 - 2 hours, Figure 92, whereas in the same system plus 1 ppm hydrocarbon the time needed for total reaction of this compound was considerably longer (Figure 93).

Perchloroethylene in Nitrogen - Approximately 1 ppm was introduced in the reaction chamber containing nitrogen. Figure 94 clearly indicates the accelerated decomposition of perchloroethylene with a peak concentration of ozone of 1 pphm O_3 . Perchloroethylene reacted to completion in this system in about 7.5 hours yielding phosgene as a decomposition product.

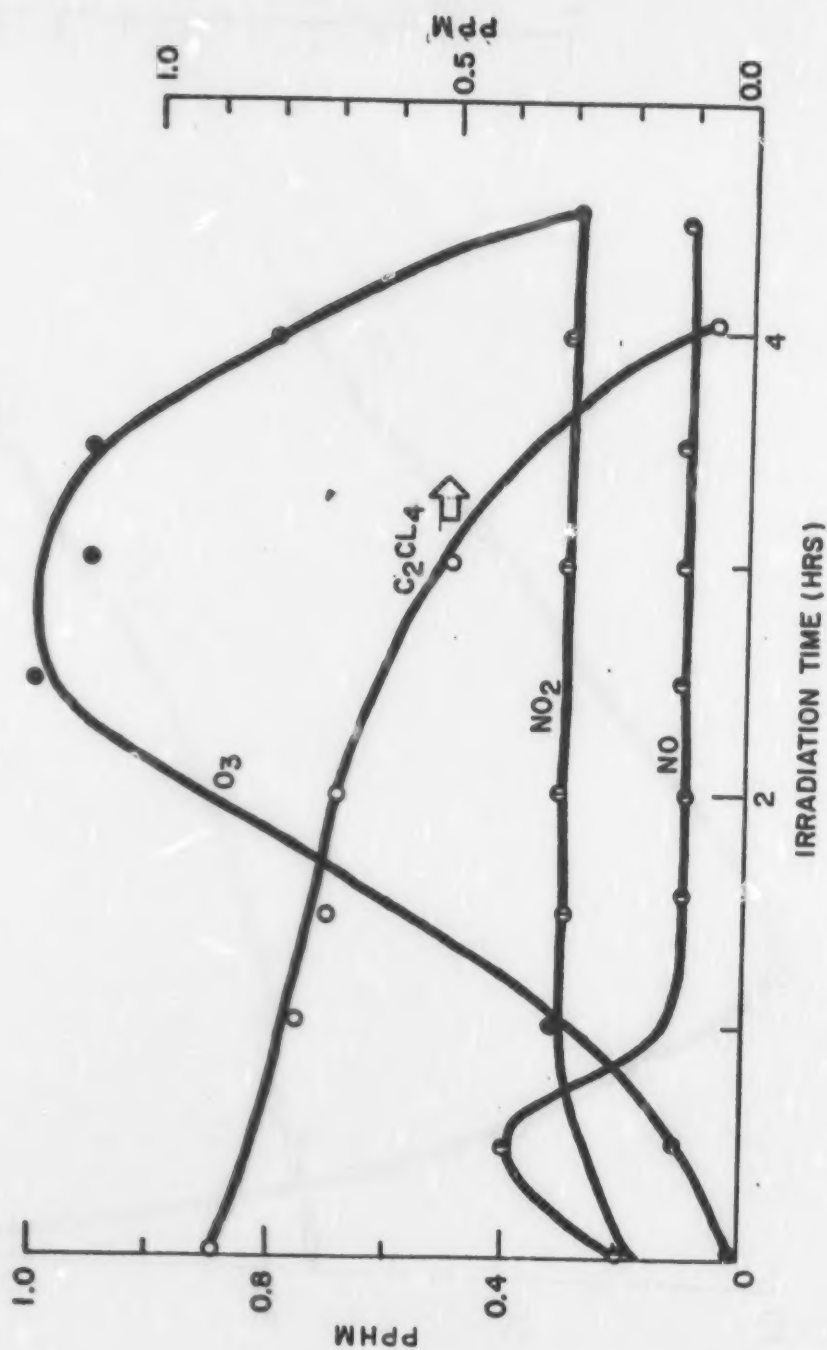
Perchloroethylene in Air at 50% R.H. plus NO_2 and Hydrocarbon "A" - Investigation of this reaction mixture indicated that the time needed for complete decomposition of perchloroethylene was between 23 and 31 hours (4 runs shown in Figures 95 - 98).

Perchloroethylene and NO_2 in Ultra Zero Air at 50% R.H. - The time needed for total reaction of perchloroethylene in this system was about 8 hours (Figure 84).

Dark Reactions in System Investigated - In all systems investigated dark reactions were conducted to verify that these compounds would not react unless supplied with the energy of the provided light source. This was accomplished by preparing identical experimental mixtures and allowing them to sit in the reaction chamber for the maximum time needed (indicated by previous experimentation) to accomplish total decomposition of the perchloroethylene if subjected to the light source. In all systems investigated concentrations of NO , NO_2 , O_3 and perchloroethylene were monitored as a function of time. The data indicated no dark reaction.

Ozone Dark Reaction - In all experiments conducted it was observed that at sometime in the course of the irradiation of the compound the ozone concentration would maximize followed by a sharp decrease in concentration. This decrease in ozone concentration was always accompanied by a significant acceleration in the rate of the perchloroethylene decomposition. It was therefore decided to investigate the possibility of an ozone attack on the perchloroethylene. This was accomplished by introducing a predetermined concentration of ozone (maximum ozone concentration observed in experimentation) in air in the reaction chamber, and by monitoring the ozone concentration as a function of time to determine the time needed for thermal decay of ozone in the system. Approximately the same amount of ozone was once again introduced into the reaction chamber with 1 ppm perchloroethylene. The ozone and perchloroethylene concentrations were monitored as a function of time. A decrease in the perchloroethylene concentration and a decrease in the decay rate of ozone (indicated by the slope) would indicate an "Ozone Attack" on the perchloroethylene,

Figure 92
C₂CL₄ IRRADIATED IN ULTRA ZERO AIR



C₂CL₄ PLUS HYDROCARBON IRRADIATED IN ULTRA ZERO AIR

Figure 95

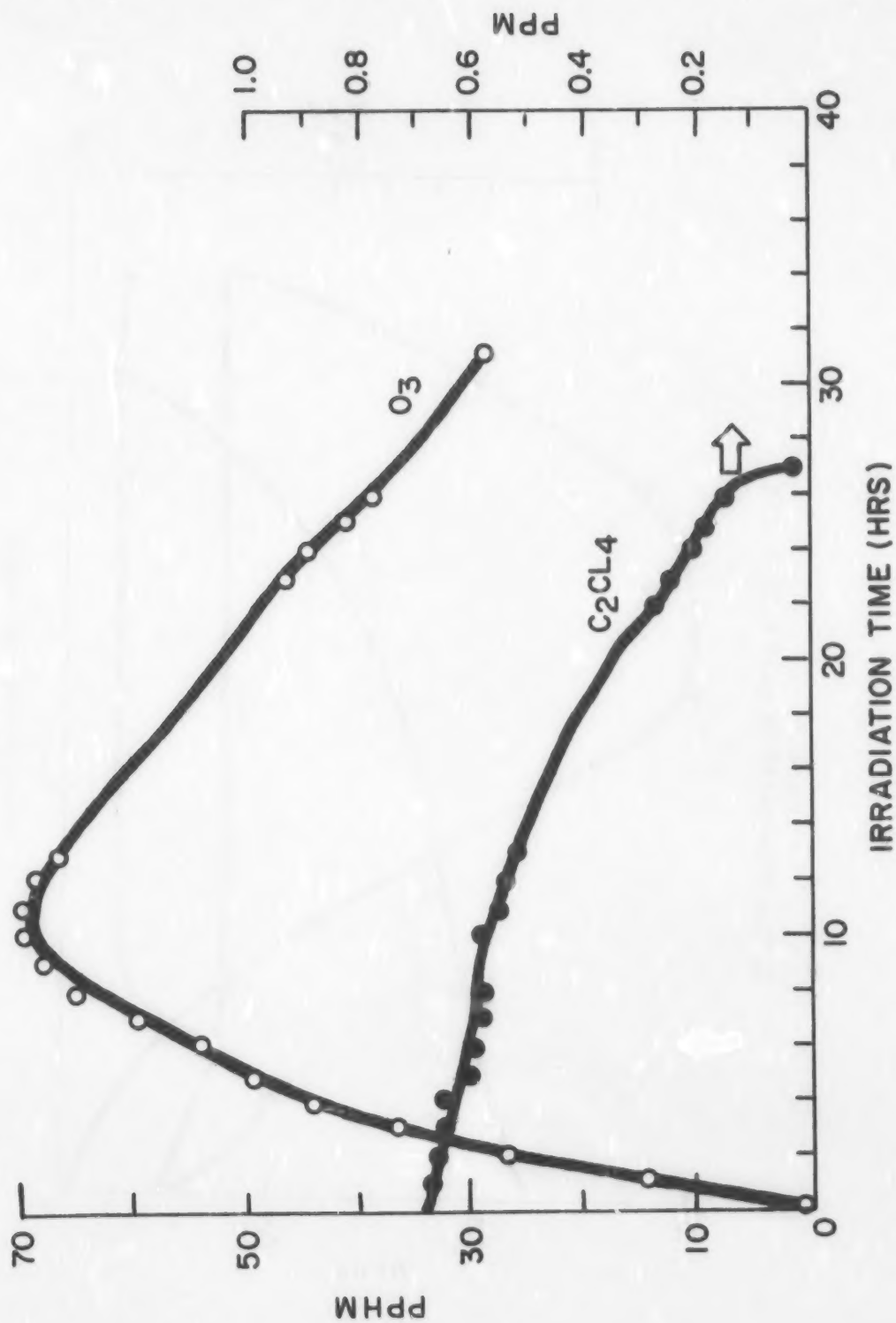
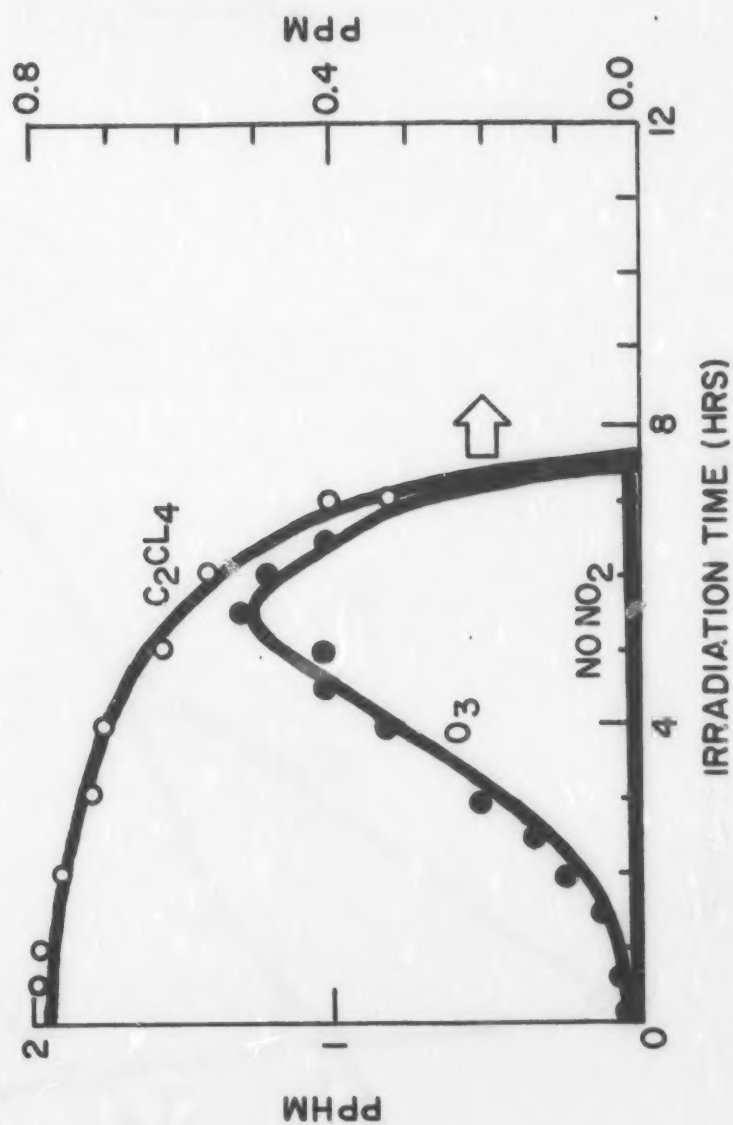


Figure 94
C₂CL₄ IRRADIATED IN NITROGEN



C₂CL₄ PLUS NITROGEN DIOXIDE AND HYDROCARBON IRRADIATED IN ULTRA ZERO AIR

Figure 95

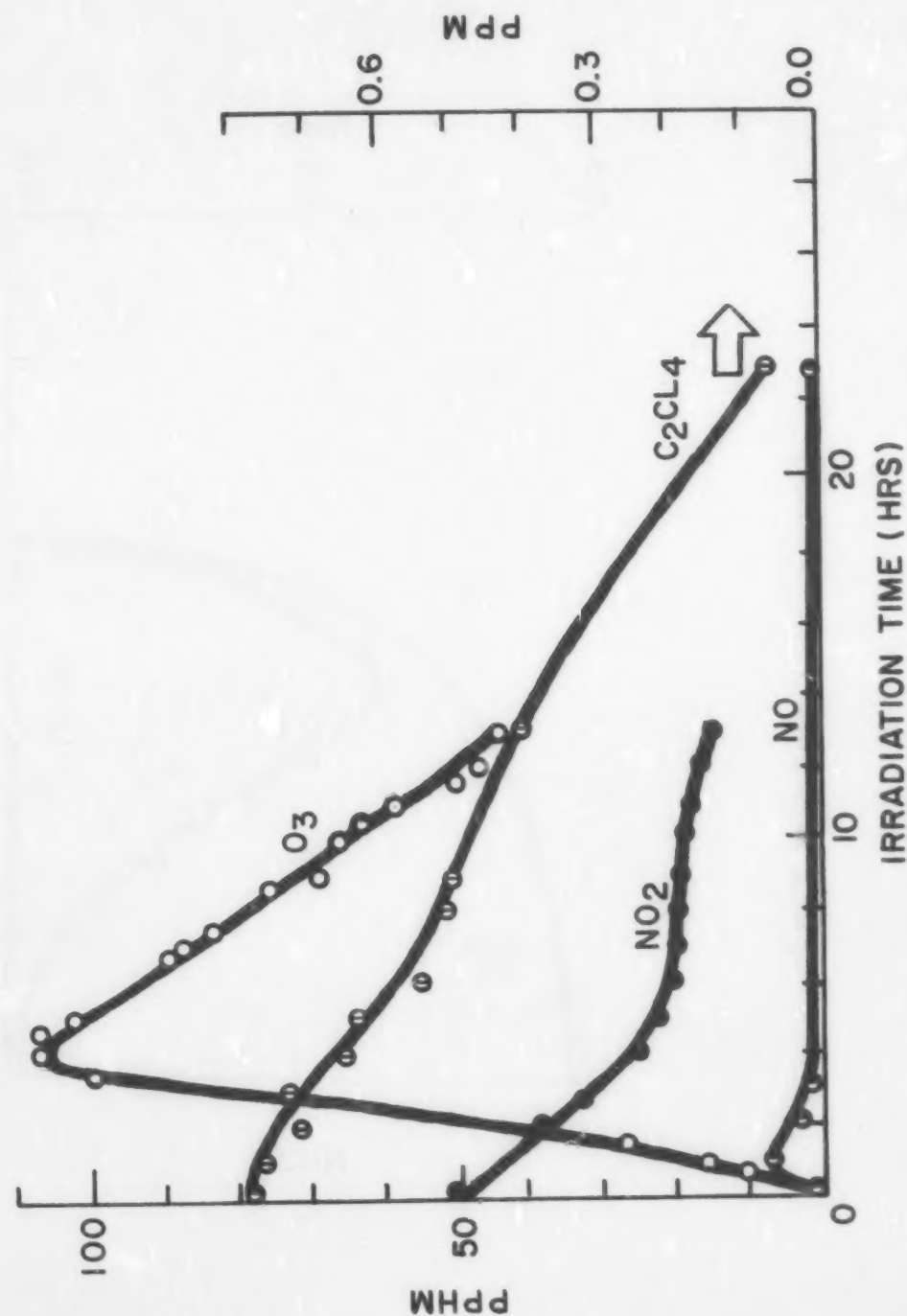
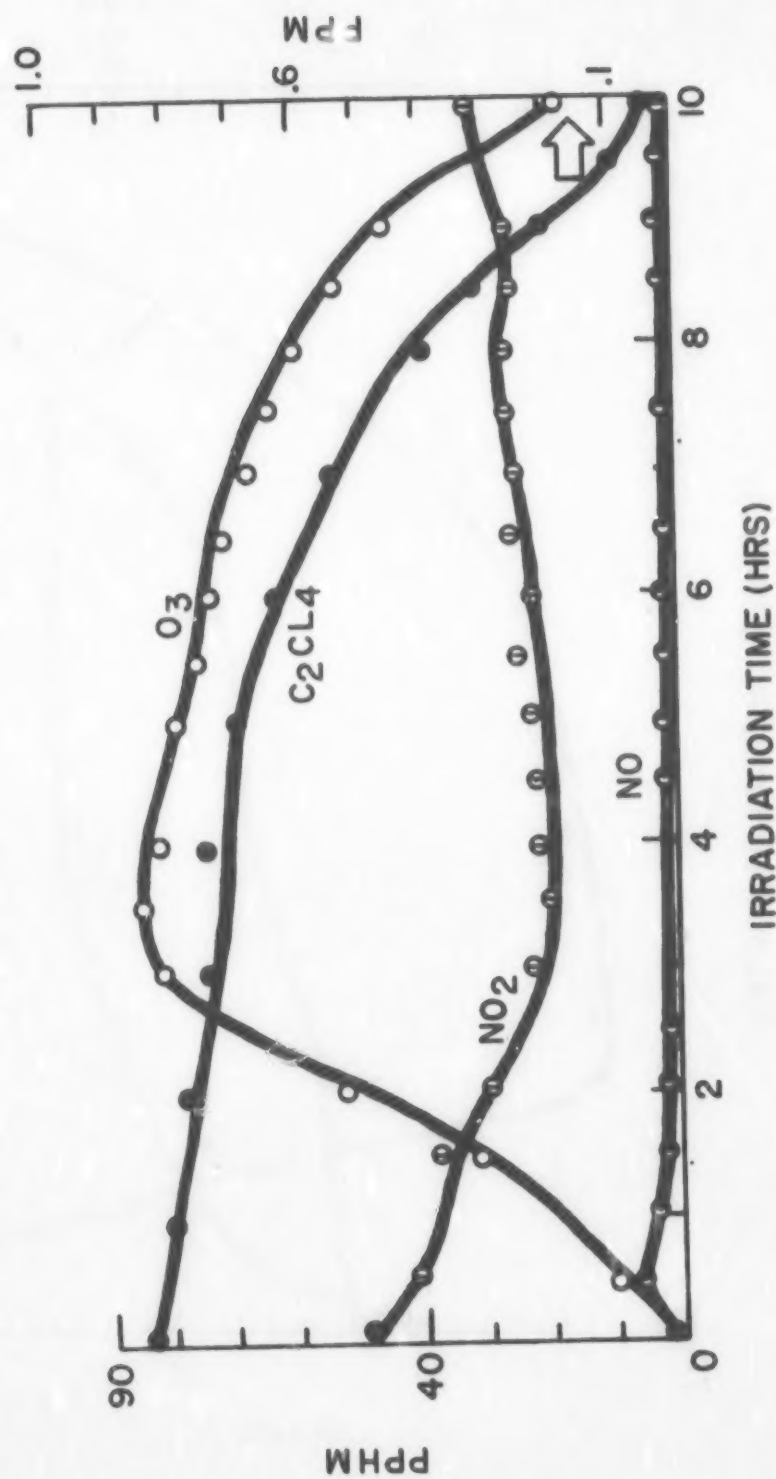
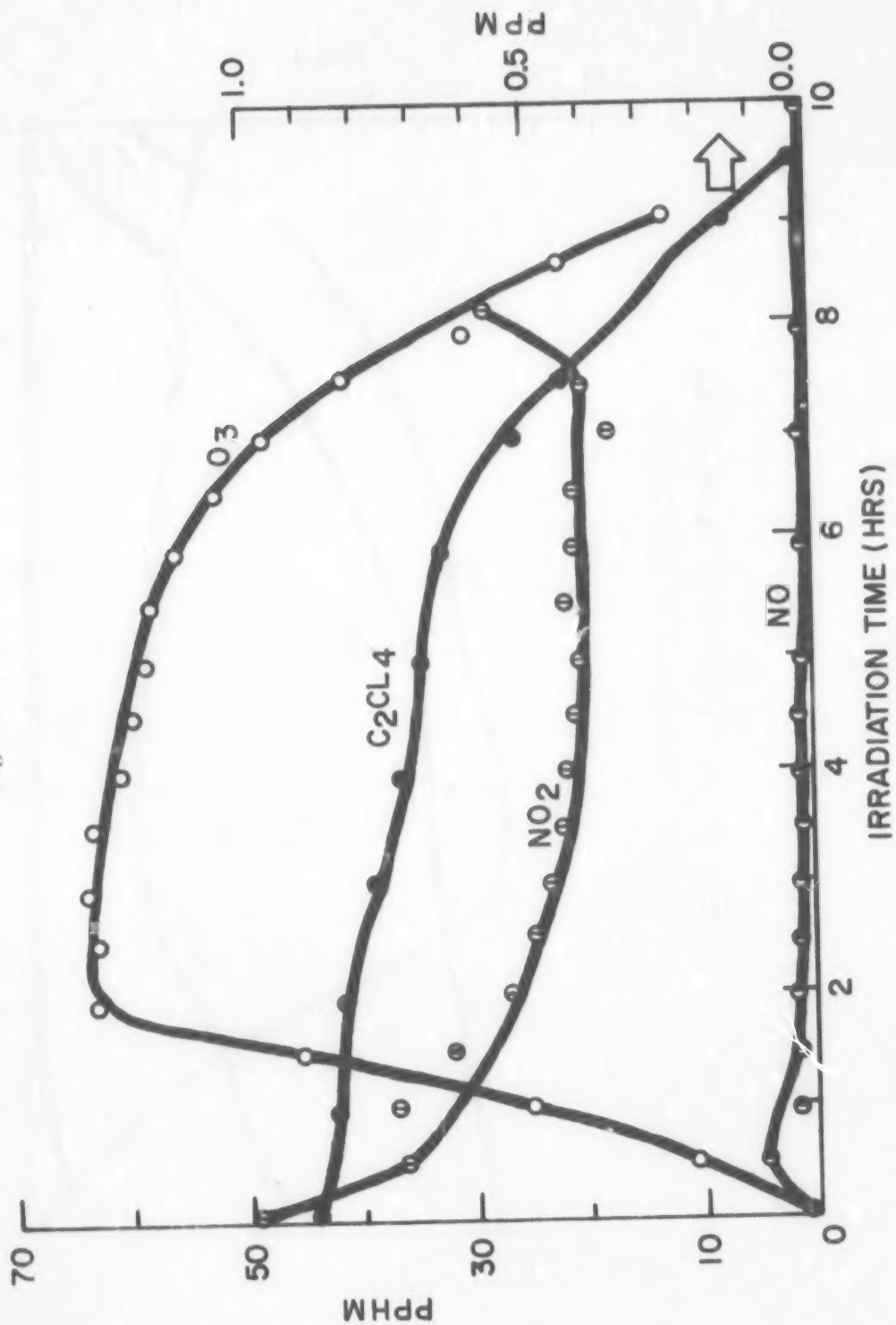


Figure 96
 C_2Cl_4 PLUS HYDROCARBON AND NO_2
 IRRADIATED IN ULTRA ZERO AIR



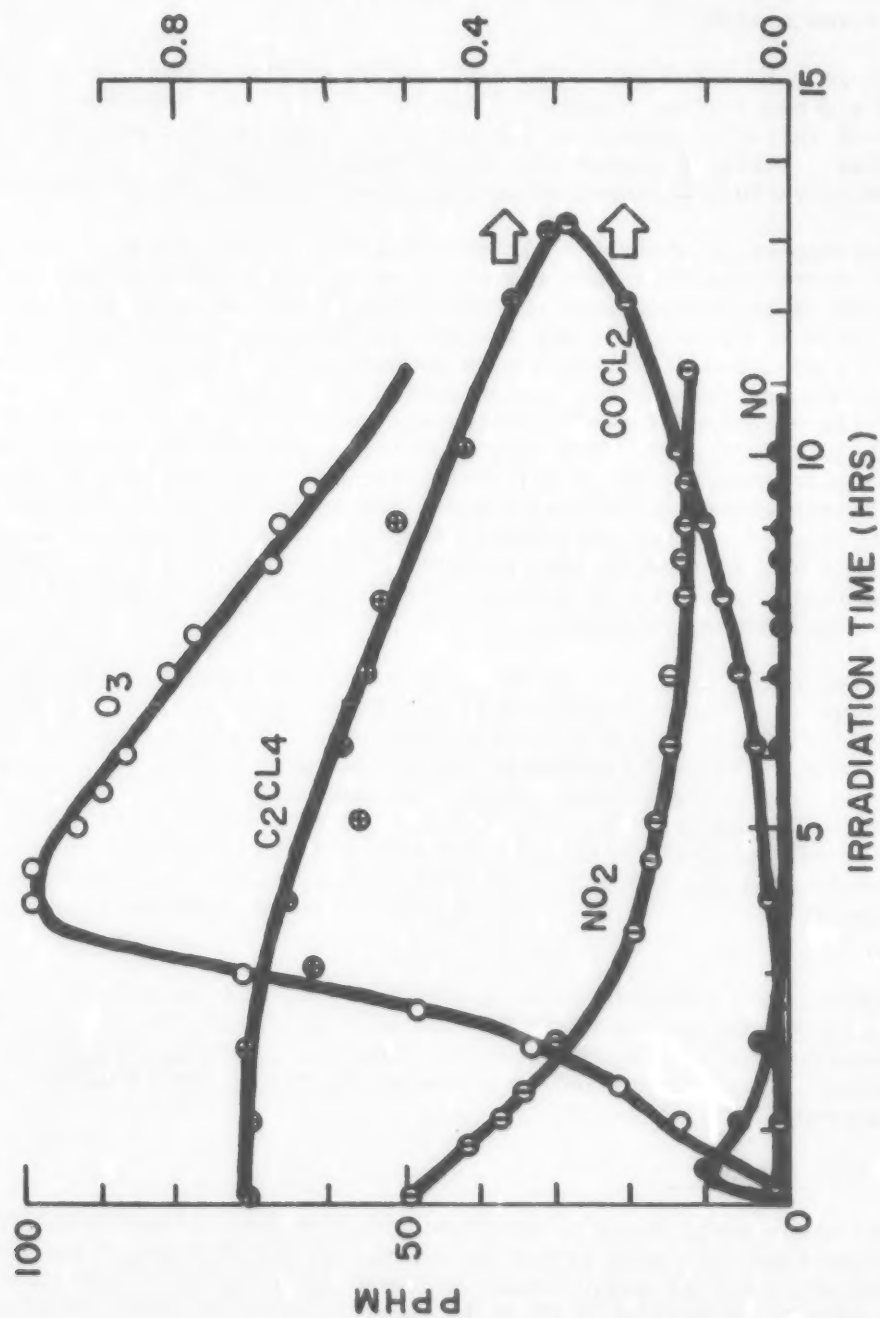
**C₂CL₄ PLUS HYDROCARBON AND NO₂
IRRADIATED IN ULTRA ZERO AIR**

Figure 97



**C₂CL₄ PLUS NITROGEN DIOXIDE
AND HYDROCARBON IRRADIATED IN ULTRA ZERO AIR**

Figure 98



and would possibly indicate one path of the mechanism of the perchloroethylene decay. The results, however (Figures 99 and 100) did not indicate this as a path in the mechanism involved in the atmospheric fate of perchloroethylene.

Phosgene as a Product - In each system studied phosgene was identified as a decomposition product. However, the rate of appearance of the compound varied depending on the particular system that was being investigated. Table 20 summarizes the systems investigated, and the phosgene concentrations measured in each system as a function of irradiation time.

Phosgene as a Catalyst - It was observed in the system of air plus perchloroethylene that once the phosgene was detectable by the gas chromatograph, perchloroethylene concentration decreased very rapidly. Because of this observation it was decided to investigate the catalytic effect (if any) induced on this system by phosgene. This was accomplished by introducing the maximum concentration of phosgene observed as a result of the reaction of perchloroethylene reaction in this system (0.8 ppm), and irradiating it for a period of time equal to the longest time needed for perchloroethylene total decomposition. Phosgene and perchloroethylene concentrations were monitored as function of irradiation time. The results of this experiment, however, indicated that no catalytic effect was exerted by the presence of the phosgene in the system, as indicated by a lack of change in perchloroethylene concentration following 2 hours irradiation.

Formation of CCl_4 - CCl_4 has been observed by us as a product during our longer runs in the simulated tropospheric irradiation of synthetic mixtures of C_2Cl_4 in air. In these and other long-term studies with other compounds, NO_2 was replenished every 24 hours. This was necessary because, in our experimental arrangement, the half-life of NO_2 was only about 6 hours (See Figure 101). Both COCl_2 and CCl_4 were identified by retention data on two separate columns (5% SE30 and 30% didecyl phthalate for COCl_2 , and 5% SE30 and 10% DC200 for CCl_4) and by their electron attachment properties^(9,5,187). The results of these experiments are presented in Table 21.

During the irradiations, an unexpected peak was tentatively identified as CHCl_2COCl and traces of CHCl_3 were also observed. While quantitative measurements of CCl_3COCl were not feasible in these preliminary experiments, it was identified as a product by the GC determination of its isopropyl ester⁽¹⁸⁴⁾.

7.2.2 Discussion -

The atmospheric fates of perchloroethylene were investigated in a variety of systems. In each system investigated, perchloroethylene under the influence of the light source employed was chemically reactive. The time needed to accomplish a given decomposition of the perchloroethylene varied significantly in repeated runs on the same system (see e.g. Figures 95 to

Table 20. Perchloroethylene Systems Investigated

System Investigated	Irradiation Time (Hour)	Perchloroethylene Concentration, PPM	Phosgene Concentration, PPM
Perchloroethylene in air @ 50% R.H.	1.5	Non-detectable by gas chromatography	.465
Perchloroethylene in air @ 50% R.H. + NO ₂	3	Non-detectable by gas chromatography	1.57
Perchloroethylene in air @ 50% R.H. + NO ₂	32	.06	.17
Perchloroethylene in air @ 50% R.H. + Hydrocarbon "A"	23	.08	.11

Table 21 Major Products of Photodissociation of C_2Cl_4 in Air

C_2Cl_4 Initial Concentration (10^{-9} v/v)	Reaction Vessels(s)	Irradiation Time (days)	Product Concentrations (10^{-9} v/v)		Weight % Conversion to CCl_4
12700	Glass	5	$COCl_2$	CCl_4	5.5
			N.V.	750	
12700	Glass	6	$COCl_2$	CCl_4	7.3
			N.V.	1000	
12700	Glass; Teflon	7	$COCl_2$	CCl_4	8.0
			18,000	1100	
750	Glass; Teflon	7	$COCl_2$	CCl_4	8.9
			900	72	
20	Teflon	7	$COCl_2$	CCl_4	7.0
			24	1.5	

Figure 99
OZONE DARK REACTIONS
OZONE PLUS C_2Cl_4
DUPLICATE RUNS

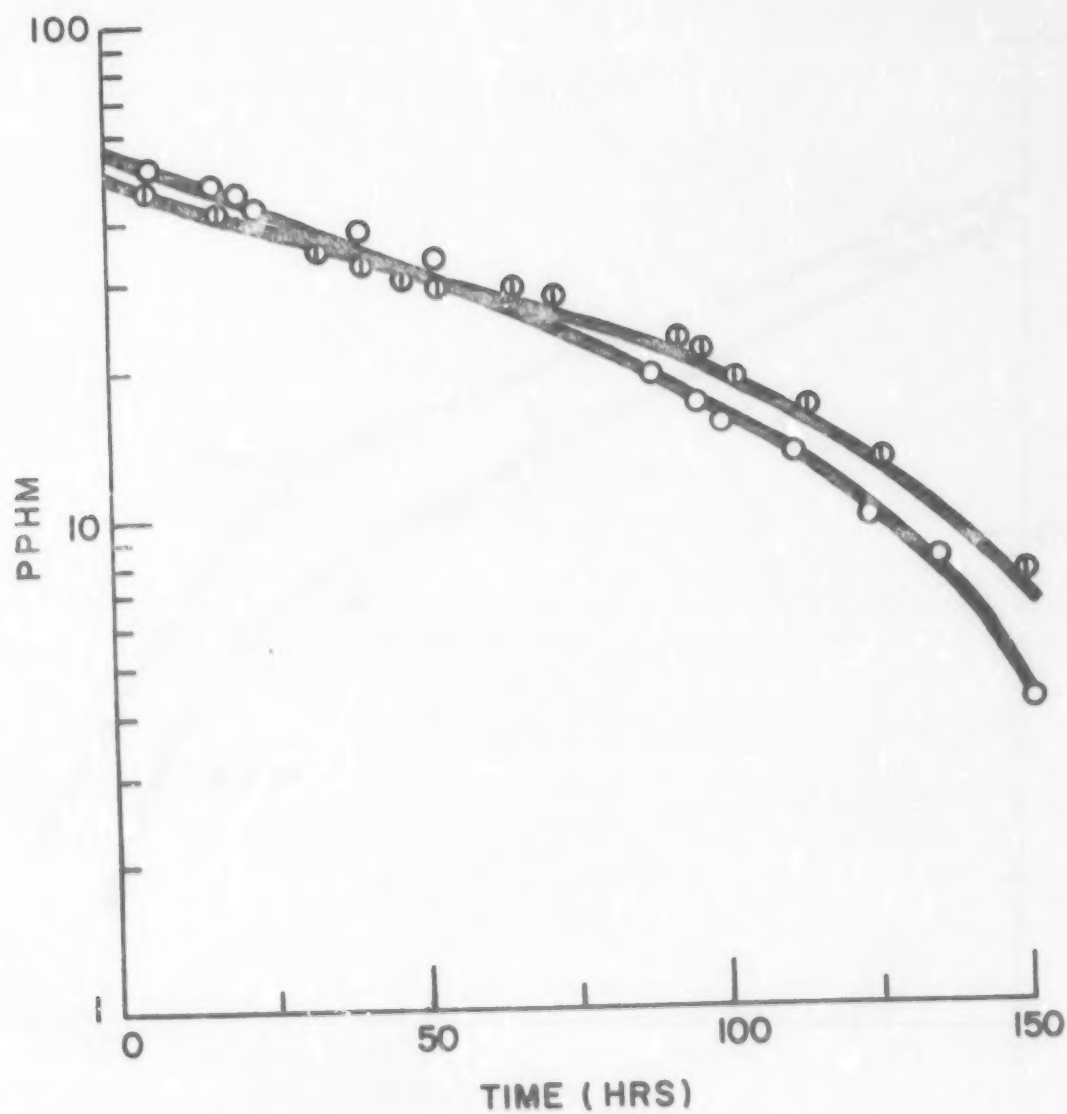
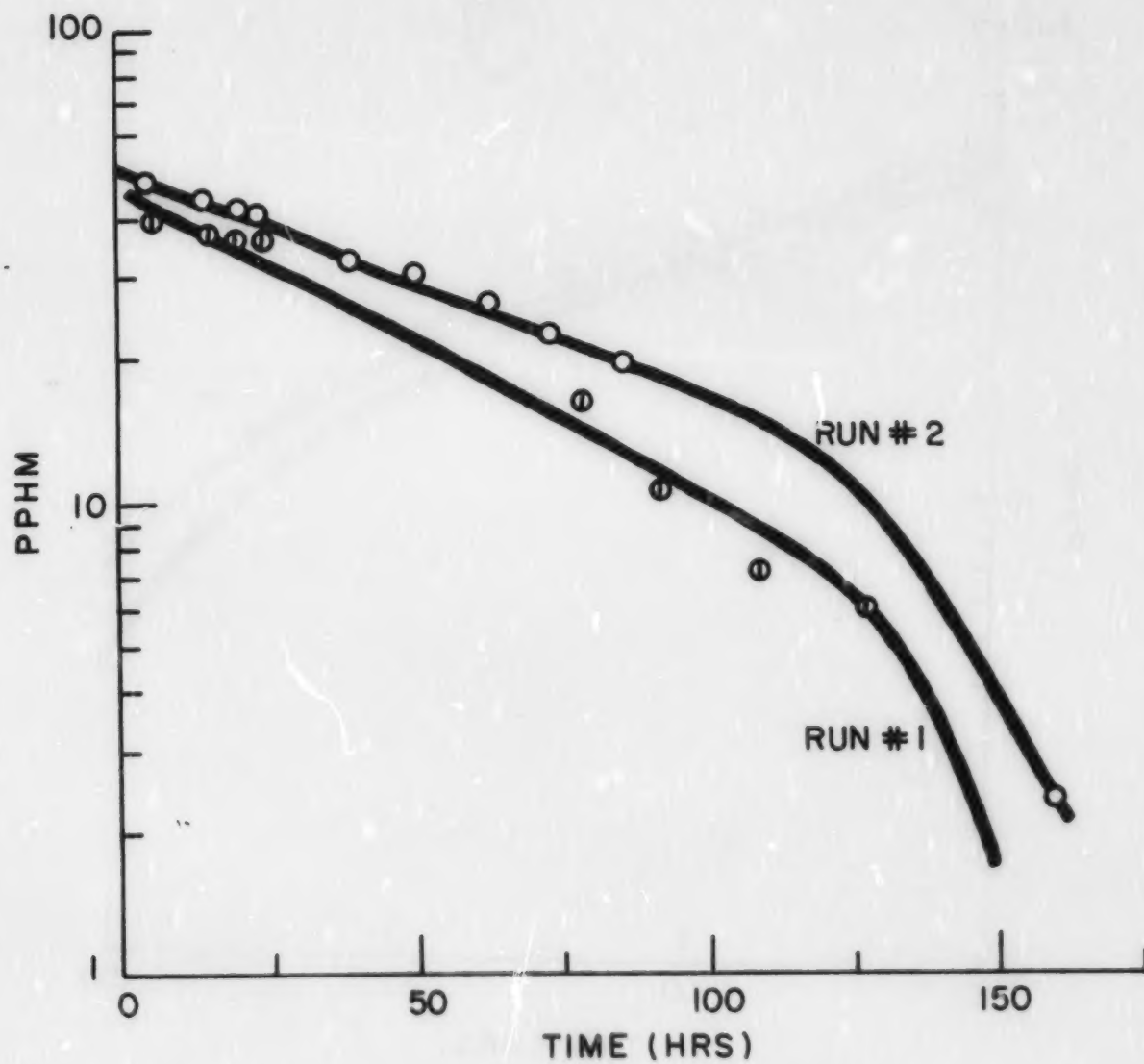


Figure 100
OZONE DARK REACTION;
DETERMINATION OF OZONE DECAY
DUPLICATE RUNS



98). Due to the highly irreproducible nature of this phenomenon, no accurate explanation can be given at this time. However, Dusoleil et al. (29) observed the same phenomenon in a series of experiments in which they investigated rate constants in gas phase photochlorination of perchloroethylene and pentachloroethylene. Such erratic results they attributed to "the time necessary for conditioning of the walls of the reaction chamber"; accomplished by the occupation of the active sites on its walls by "perhaps" polymeric chlorinated derivatives. As a result of this phenomenon they discarded a number of their initial experimental results which were erratic in terms of total time needed for 100% decomposition of the compounds of interest.

None of the experimental results obtained by us were discarded, since the primary objective of the derived experimental scheme was to indicate the fates of these compounds in a polluted atmosphere. It was felt that the variable nature of the decomposition kinetics were not as important to an understanding of air pollution phenomenon as the observations that C_2Cl_4 did decompose under simulated tropospheric conditions, and the general behavior of the other reactants, intermediates and products.

Carbon Tetrachloride and Trichloroacetylchloride Formation - A maximum concentration of 72 ppb carbon tetrachloride was measured as a decomposition product of the induced perchloroethylene chemical reactions. This was observed and measured in a mixture of air plus perchloroethylene which had been subjected to the irradiating light source for 63 hours. The same mixture was monitored for trichloroacetylchloride, and this compound was positively identified as a decomposition product by the method previously explained. CCl_4 concentrations continued to increase well after all the C_2Cl_4 had reacted while the $COCl_2$ and $CHCl_2COCl$ concentrations plateaued. At the same time CCl_3COCl continued to react suggesting its role as the CCl_4 precursor. The overall reaction is probably initiated by photolysis of C_2Cl_4 followed by a chlorine sensitized photo-oxidation (23).

From Table 21 on the average, C_2Cl_4 photodecomposition leads in 7 days to the formation by weight of about 8% CCl_4 and 70 to 85% of phosgene. Since the present world-wide emissions of C_2Cl_4 can be estimated to be about 450 millions kg/yr. (192), this conversion would result in an annual atmospheric CCl_4 loading of 36 millions Kg/yr.

This source of CCl_4 alone can account, depending on the residence time, for a significant fraction of the atmospheric CCl_4 budget. In any consideration of the CCl_4 budget, this source must be considered along with others such as direct industrial emission and possibly methane/chlorine reactions (10).

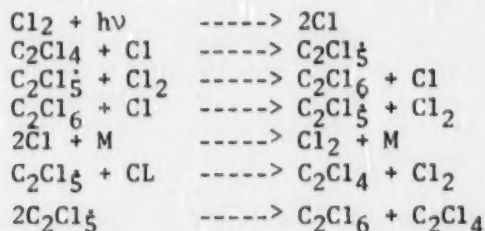
Our laboratory simulation studies indicate that CCl_4 is tropospherically stable (see Section 7.4.1 below). Reactions such as $CCl_4 + OH \rightarrow HOC1 + CCl_3$ or $CCl_4 + O \rightarrow COCl_2 + Cl_2$ (1,193), are negligible under all tropospheric conditions. Given the relative inertness of CCl_4 , another possible precursor of ozone destroying stratospheric chlorine atoms (1) presents itself in the form of CCl_4 as a secondary anthropogenic pollutant.

It is significant too that a relatively innocuous material such as C_2Cl_4 (A.C.G.I.H. T.L.V. 100 ppm) can decompose in the atmosphere to produce highly toxic materials such as phosgene (Proposed A.C.G.I.H. T.L.V. revision 0.05 ppm).

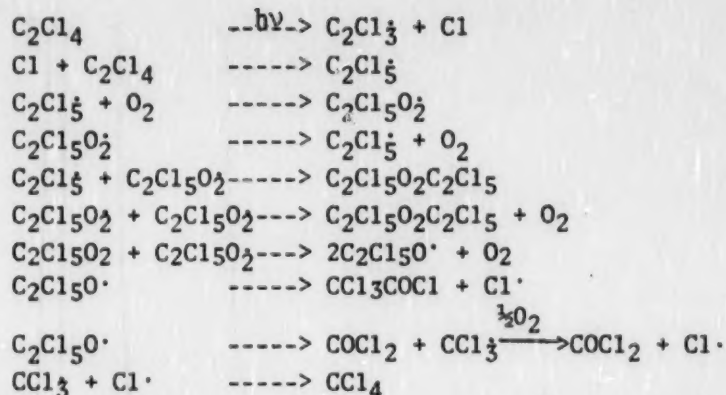
Ozone Concentration - In all systems studied, it was observed that the ozone concentration would maximize after some given time of exposure of the system to the light source. The ozone concentration would then decrease with a simultaneous decrease in the concentration of perchloroethylene in the system and an increase in the rate of phosgene production (see Figure 98). In the system investigated in which hydrocarbon "A" was incorporated it was observed that:

- (a) Ozone concentration increased at a slower rate than in any of the systems investigated, and decreased beyond its maximum more slowly.
- (b) The reaction rate of perchloroethylene was substantially reduced.
- (c) The time needed for 96 to 100% decomposition of perchloroethylene was substantially increased.
- (d) The observed ozone concentration was substantially greater than that observed in any other system investigated.

Possible Reaction Mechanism for C_2Cl_4 - There are no documentations of simulated smog chamber studies performed on perchloroethylene. However, gas phase photochlorination studied performed using intermittent light capable of inducing chemical reactions have been performed on mixtures of perchloroethylene with Cl_2 in air⁽²⁶⁾ in which the following scheme was proposed as the initiator in the observed chemical reactions of perchloroethylene.

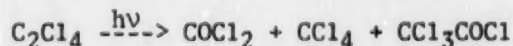


They also established the fact that reaction with impurities on the walls or other entities (Cl_3 , polymeric chlorinated derivatives needed to occupy sites on the walls of the reaction chamber) were, within a highly experimental precision, completely negligible. Although the experimental scheme studied by this investigator did not involve introduction of chlorine in the reaction chamber, the writer proposes a chlorine sensitized oxidation of perchloroethylene, initiated somewhat differently from that proposed by Dusoleil et al., but including some of his proposed paths. The proposed mechanism is as follows:



As is clearly indicated by the proposed mechanism there is a time lag necessary for the initiation and propagation of the radical-chlorine, radical-oxygen and radical-radical species. Figure 92 indicates a time lag followed by a rapid decomposition of perchloroethylene. In the systems investigated in which hydrocarbon is introduced there is an extensive initial time lag before perchloroethylene begins to react chemically, and this is followed by a slow reaction rate. This can be explained by the fact that the very reactive olefin radicals not only compete with the C_2Cl_4 for the C_2Cl_5 specie but also probably react rapidly with the Cl chain carrier itself. This proposed path would be followed until the olefinic specie from the hydrocarbons has been totally reacted. Then the perchloroethylene would be attacked by the Cl specie, hence the observed extended time lag in the hydrocarbon system. An additional explanation could involve collisional de-excitation of the C_2Cl_4^* with olefin, resulting in a photosensitized dissociation of the latter.

Step 8 in the proposed reaction scheme was substantiated by identifying trichloroacetylchloride with extended irradiation time of 24 hours. It was observed that the trichloroacetylchloride had been completely decomposed and the concentration of carbon tetrachloride had increased considerably. The overall reaction scheme may be presented to proceed as follows by consecutive or side reactions:



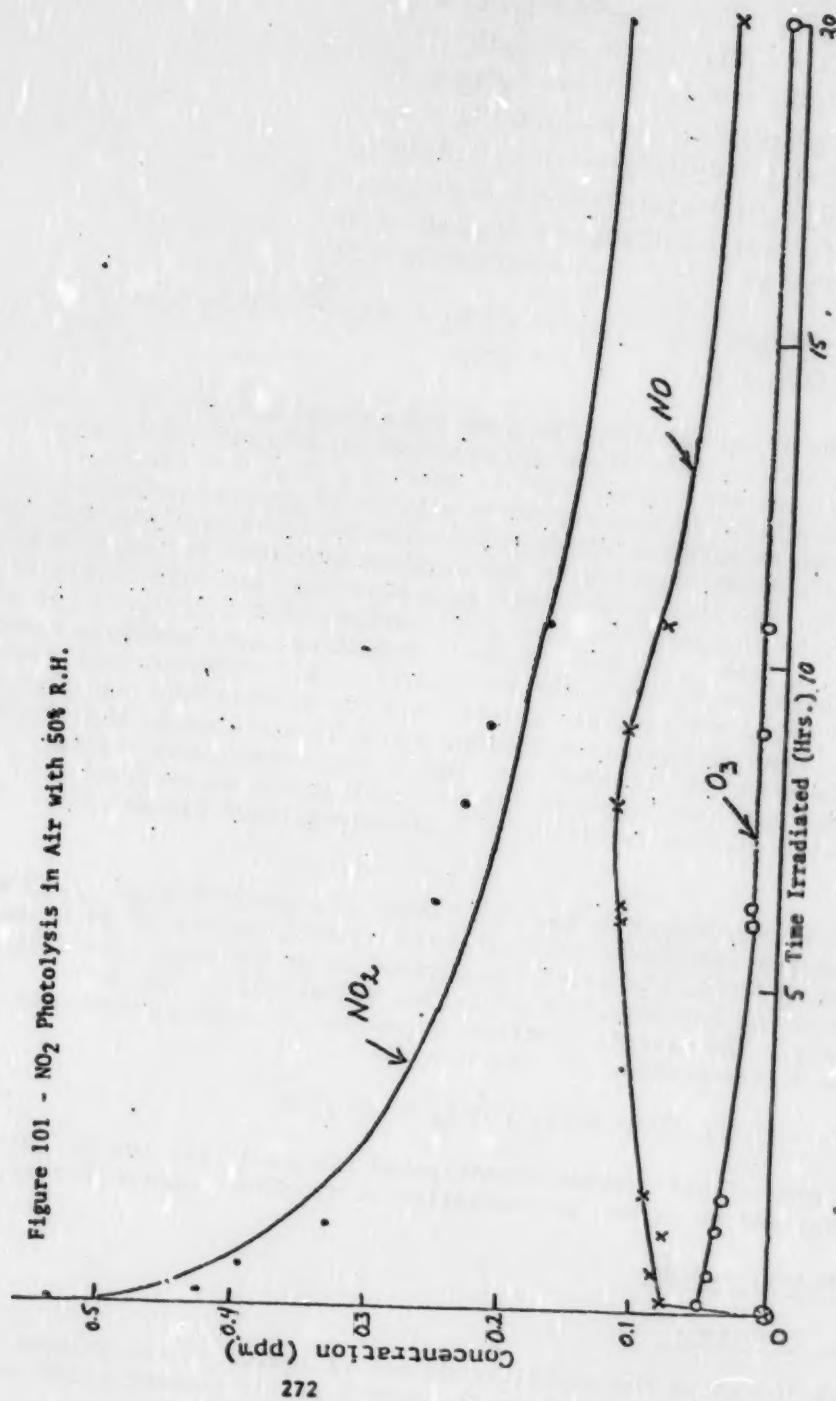
Blank runs of all systems investigated produced very low NO, NO₂ and O₃ readings and no carbon tetrachloride or trichloroacetylchloride.

7.3 Methyl Iodide

7.3.1 Results -

Figure 102 shows the stability of methyl iodide in the presence of ozone which decays thermally while the methyl iodide concentration remains the same.

Figure 101 - NO_2 Photolysis in Air with 50% R.H.



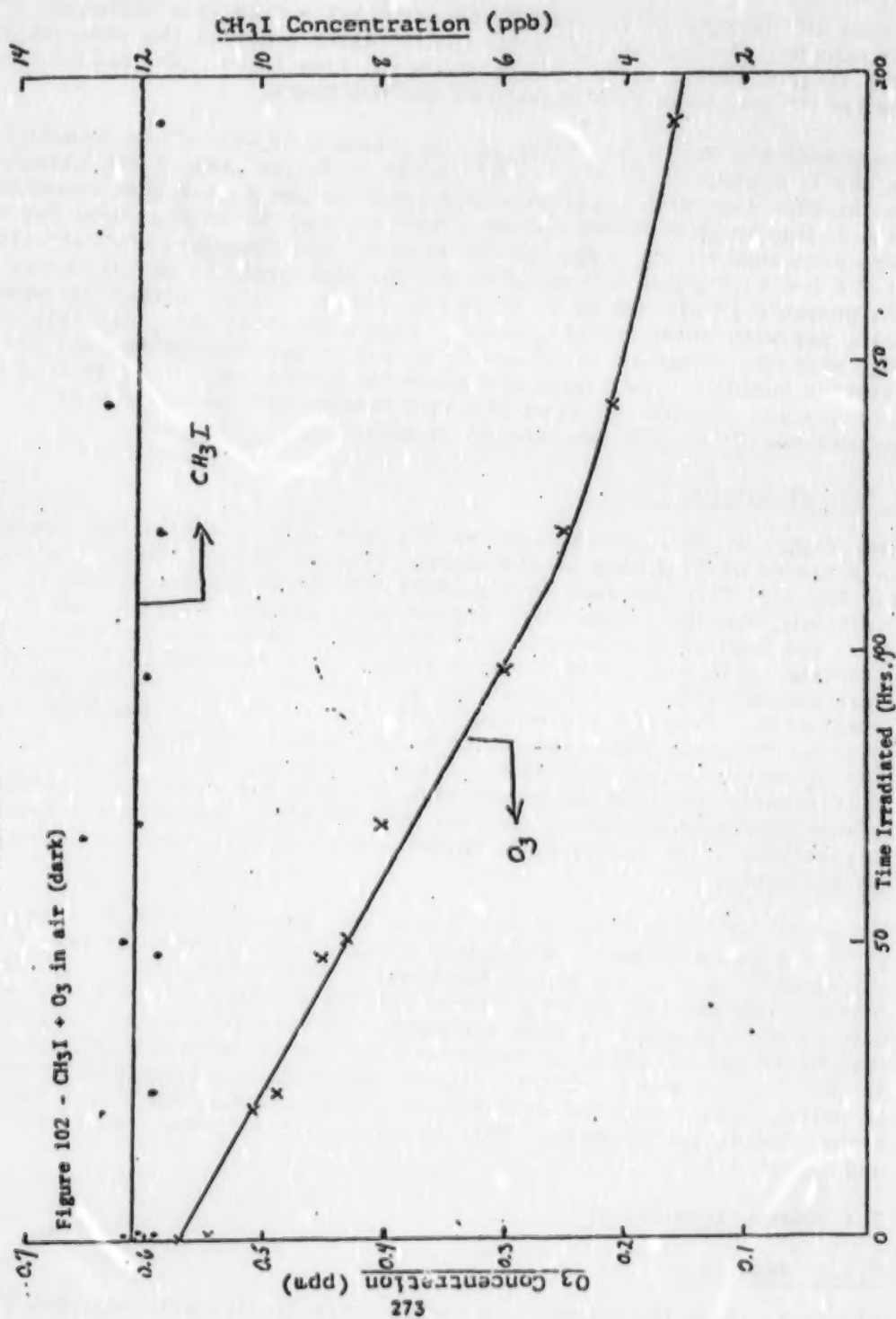


Figure 103 represents the photolysis of methyl iodide in a nitrogen atmosphere. The photolysis is apparently first order as the straight line plot (Figure 104), of the concentration vs. time shows. The half-life of the methyl iodide in this experiment was 6.5 hours.

The photolysis of methyl iodide in the presence of oxygen, as pointed out in the literature^(46,49,50,51,194) should be faster than in its absence due to the fact that methyl radicals react with oxygen rather than recombine with iodine to form methyl iodide. However, the Teflon bags used for runs were permeable to the oxygen in the room air and therefore the half-life of 7.6 hours (Figures 105 and 106) for the photolysis of methyl iodide in the presence of air and water is in disagreement with neither the previous value nor with other investigations. Figure 85 shows the photolysis of CH_3I with the formation of NO and O_3 in air in presence of NO_2 and 50% relative humidity, and Figure 107 shows the first-order decay of CH_3I in this system. Figure 108 shows the same measurements when 1 ppm of hydrocarbon ("Fuel A") was present in addition.

7.3.2 Discussion -

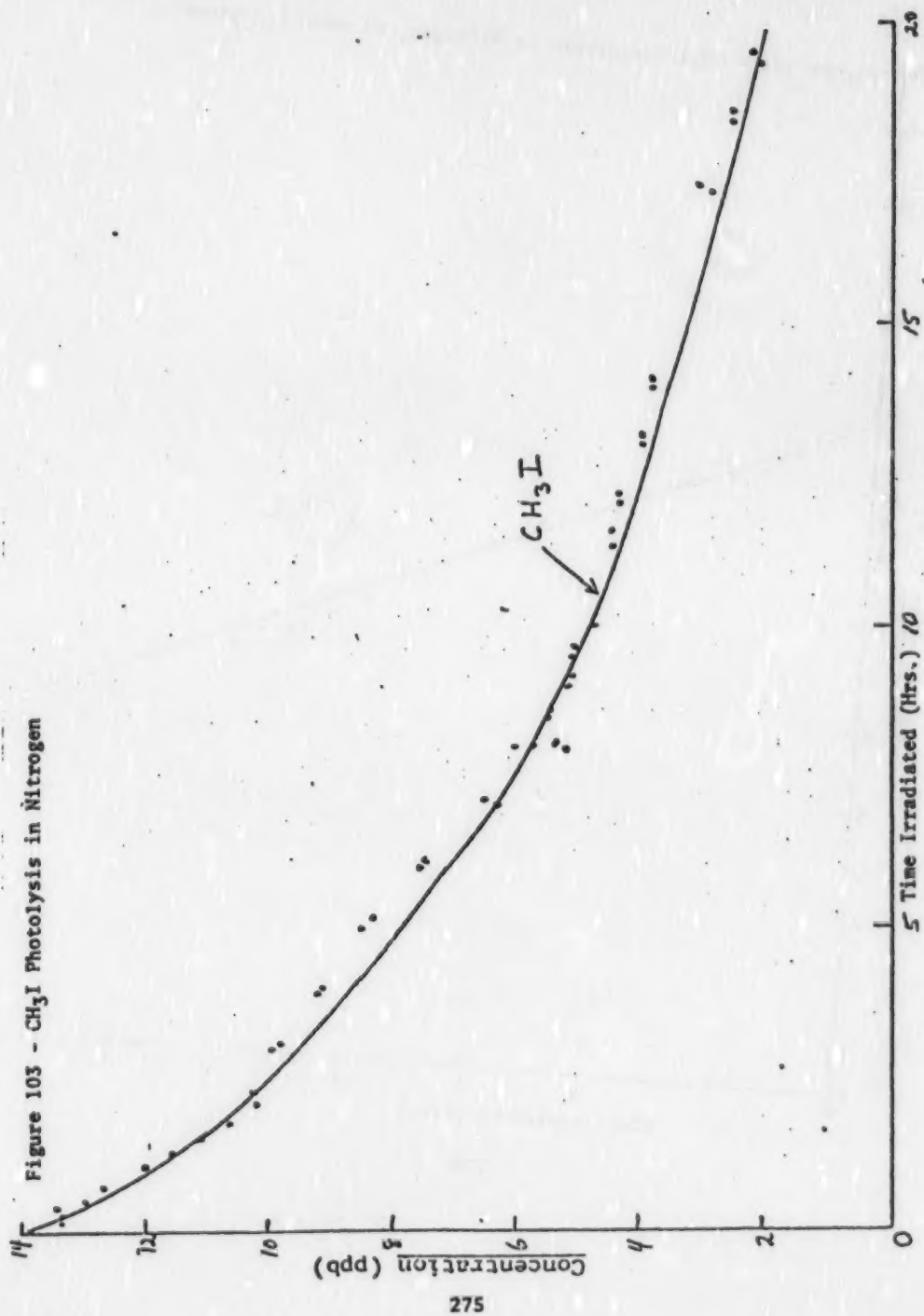
From Figure 85 it is clear that the NO_2 half-life in air is much smaller in presence of CH_3I than in its absence (Figure 101). With CH_3I present, the NO_2 half-life was less than 2 hours and the NO reached a peak of 0.175 ppm, whereas in the blank the maximum nitric oxide value was 0.120 ppm. the initial concentrations of nitrogen dioxide were respectively 0.450 and 0.535 ppm. Note that the nitric oxide remained at a steady-state concentration in the blank but was consumed in the methyl iodide irradiation. From the literature^(41,43,195) nitric oxide has been shown to be an extremely efficient scavenger for methyl radicals. The half-life of methyl iodide is a fast 3.6 hours (Figure 107) due to the inhibition by nitric oxide of the back reaction reforming methyl iodide. Hydrocarbons seem to negate the influence of nitric oxide on the reaction (Figure 108). The half-life of methyl iodide in this simulated urban air was 5.5 hours.

The source of atmospheric methyl iodide has been postulated by Lovelock et al.⁽¹⁰⁾ to be the oceans. Biological methylation of iodine by marine plants and animals is a likely cog in the wheel of the iodine cycle. Another possible way the sea can be a source for methyl iodide is by methyl radicals in the air reacting with sea salts. To test this possibility, a mixture of 12 ppm of potassium iodide and 1.0 ppm of acetone were irradiated in the 72 liter pyrex reactor. Almost immediately a four-fold increase in methyl iodide over the unirradiated blank to a maximum of 1.4 ppm of methyl iodide was observed. This result agrees with experiments of Pitts and Blacet⁽¹⁹⁵⁾.

7.4 Carbon Tetrachloride

7.4.1 Results -

Figure 83 shows the reaction of carbon tetrachloride with nitrogen oxides,



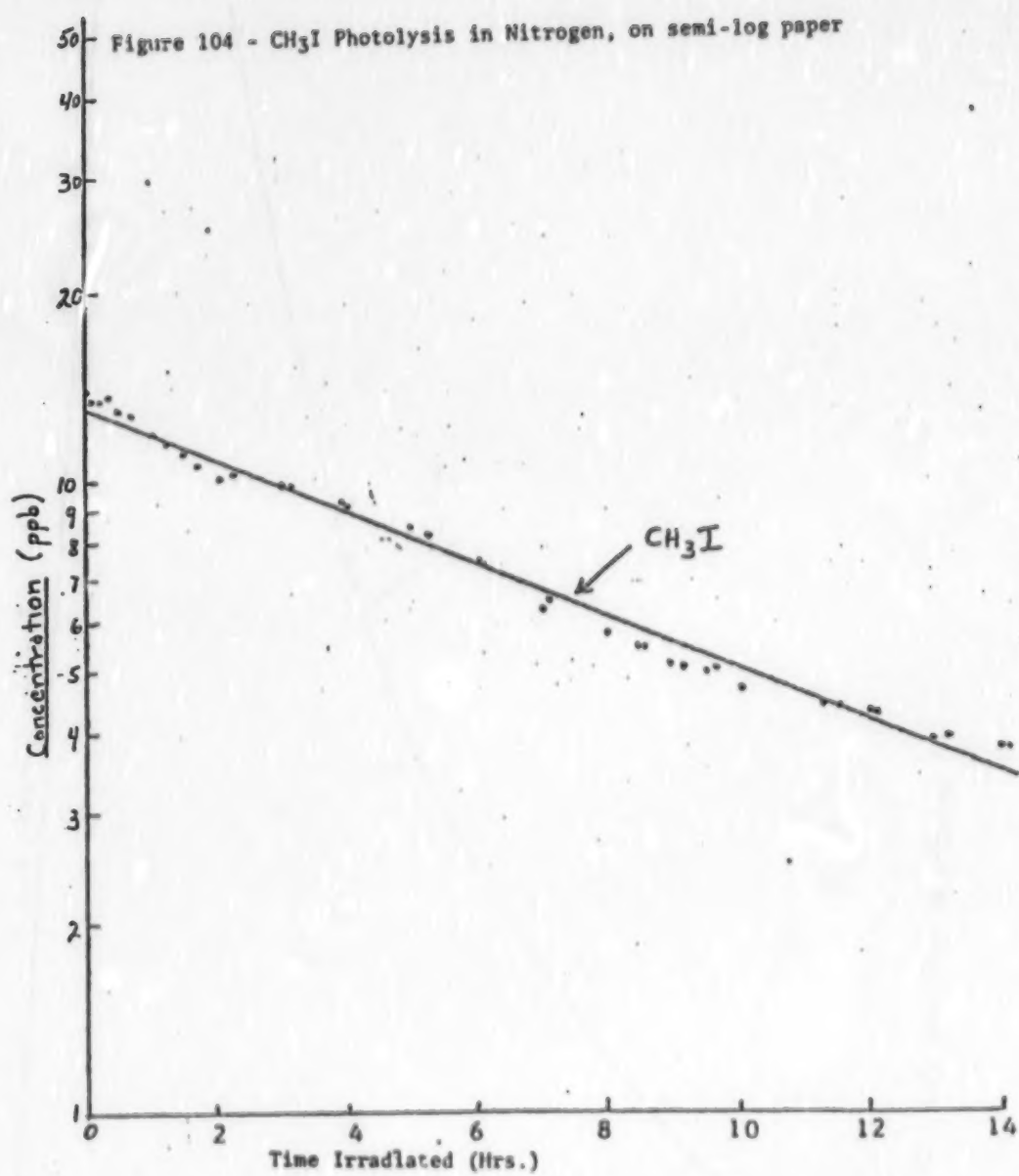
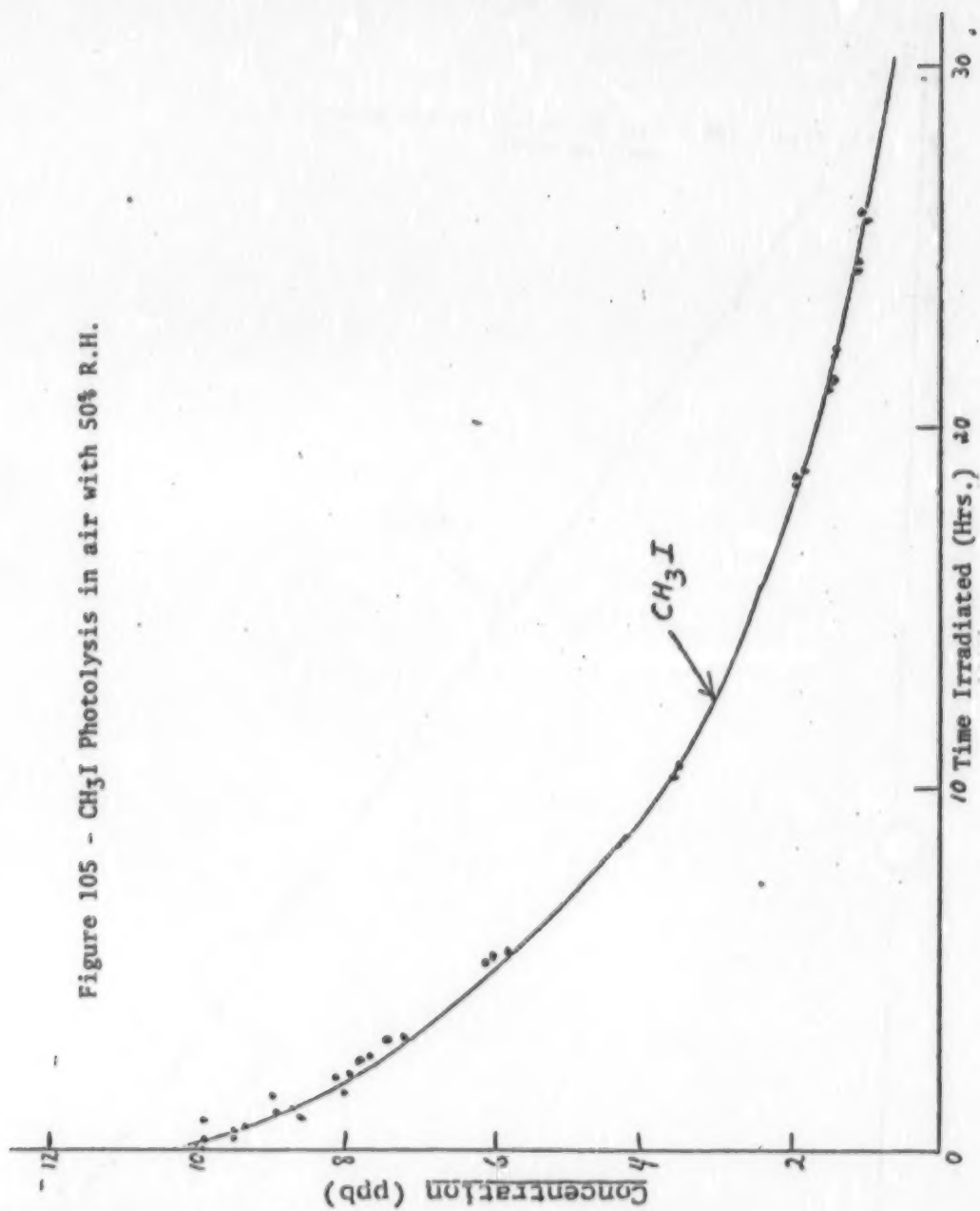
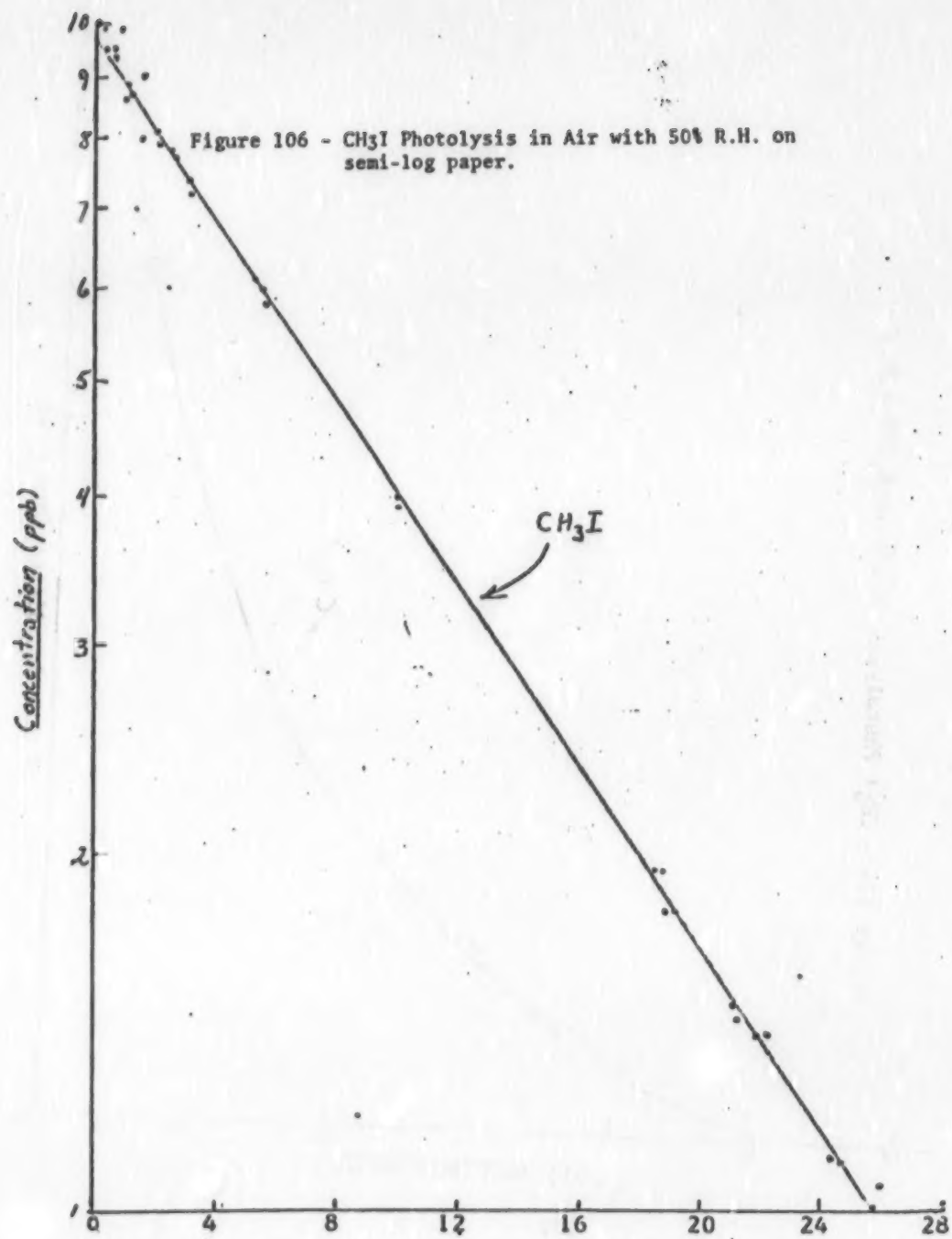
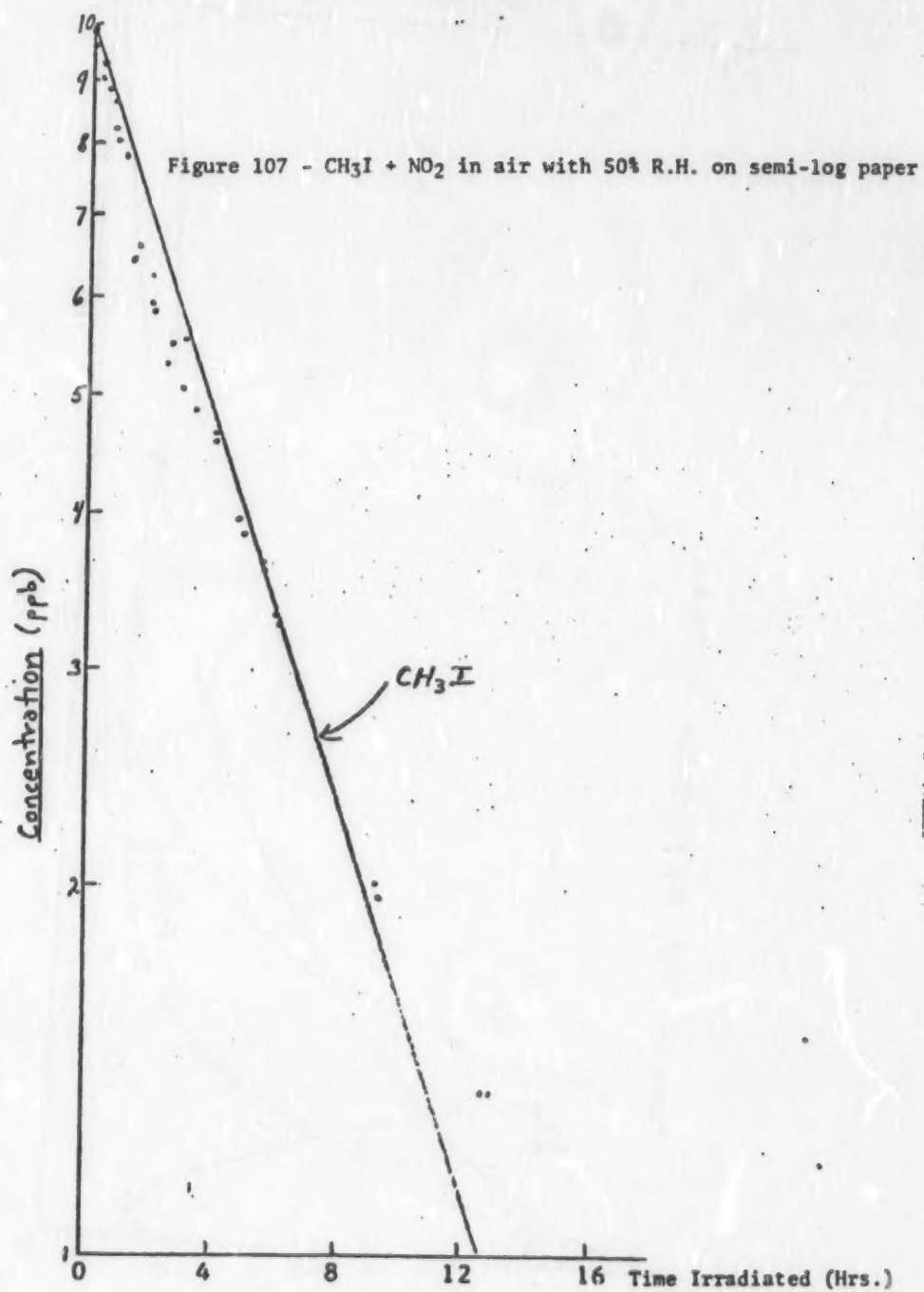
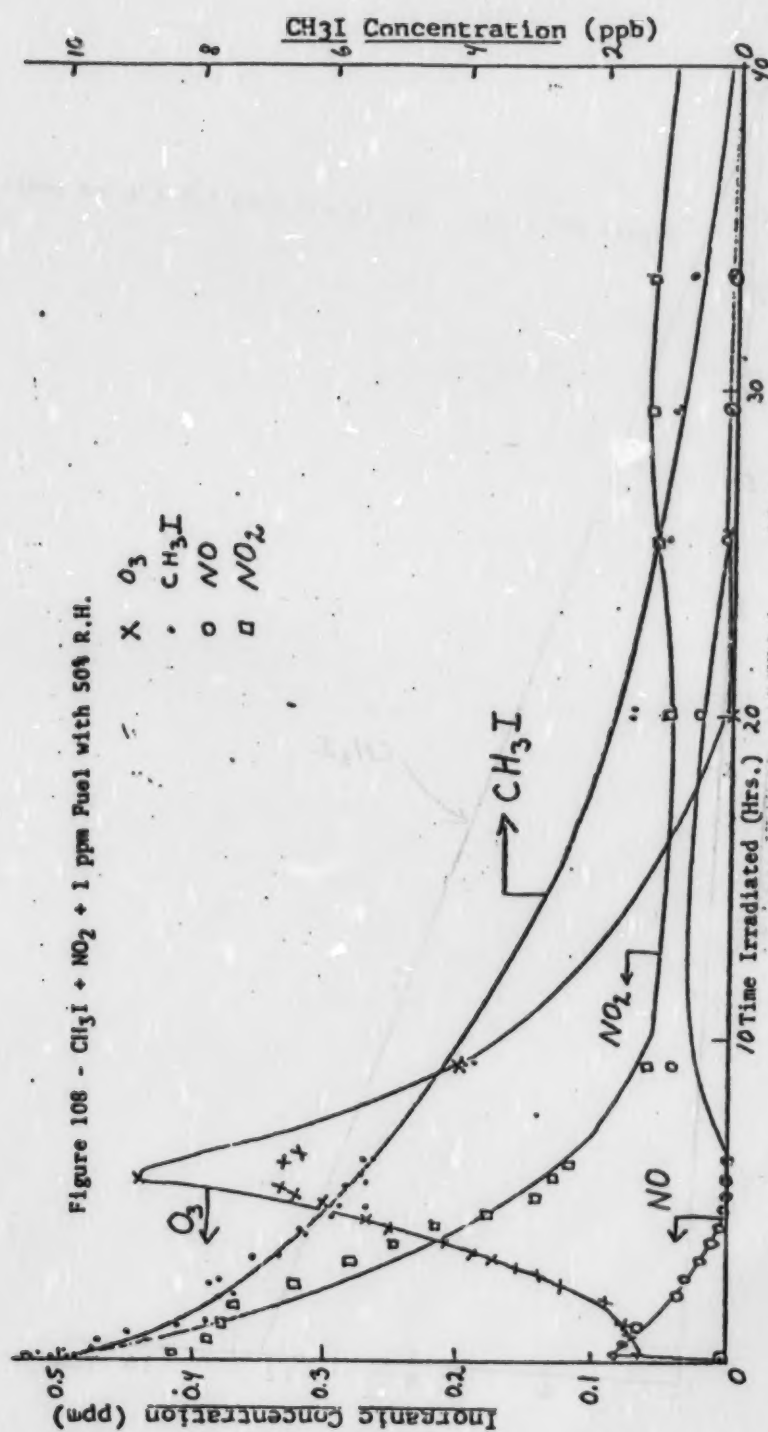


Figure 105 - CH_3I Photolysis in air with 50% R.H.









ozone, atomic oxygen and simulated tropospheric sunlight in a Mylar bag. The compound remained stable for more than 200 hours. The chamber was replenished daily with nitrogen dioxide to bring the chamber to a 0.5 ppm concentration providing a constant supply of reactive constituents for attacking the halocarbon.

Figure 109 depicts the stability of carbon tetrachloride from the attacks of free radical hydrocarbons as well as ozone, atomic oxygen and nitrogen oxides. Here too, nitrogen dioxide was replenished daily.

Having established the tropospheric stability of CCl_4 , its possible stratospheric reactivity was investigated. Figure 90 includes its decay under the influence of U.V. irradiation in ppb mixture in air. Its half-life under our conditions of 5.5 minutes corresponds to a minimum half-life in the stratosphere of 37 hours.

7.4.2 Discussion -

From the data presented above it can be inferred that carbon tetrachloride will not decompose in the troposphere. It is clear, however, that CCl_4 will play a role similar to that ascribed to CCl_3F and CCl_2F_2 as precursors of chlorine atoms potentially destructive to stratospheric ozone.

7.5 1:1:1 Trichloroethylene

7.5.1 Results -

Figure 109 shows the reaction of 1:1:1-trichloroethane with nitrogen oxides, ozone, atomic oxygen, free radicals and simulated tropospheric sunlight in a Mylar bag. The compound remained stable for more than 200 hours. The chamber was replenished daily with nitrogen dioxide to bring the chamber to a 0.5 ppm concentration, providing a constant supply of reactive constituents for attacking the halocarbon.

7.5.2 Discussion -

From these systems, it can be inferred that methyl chloroform will not decompose in the troposphere. We have not tested its stability to stratospheric conditions.

7.6 Trichloroethylene

7.6.1 Results -

Figure 110 illustrates the stability of T.C.E. to thermal attack by ozone. Figure 111 shows the effect of irradiating this compound with simulated tropospheric sunlight in nitrogen. The effect of the presence of air and 50% relative humidity are shown in Figure 112. With the addition of NO_2 to the reaction mixture the results shown in Figure 113 were obtained. Figure 114 shows the results when both NO_2 and hydrocarbon

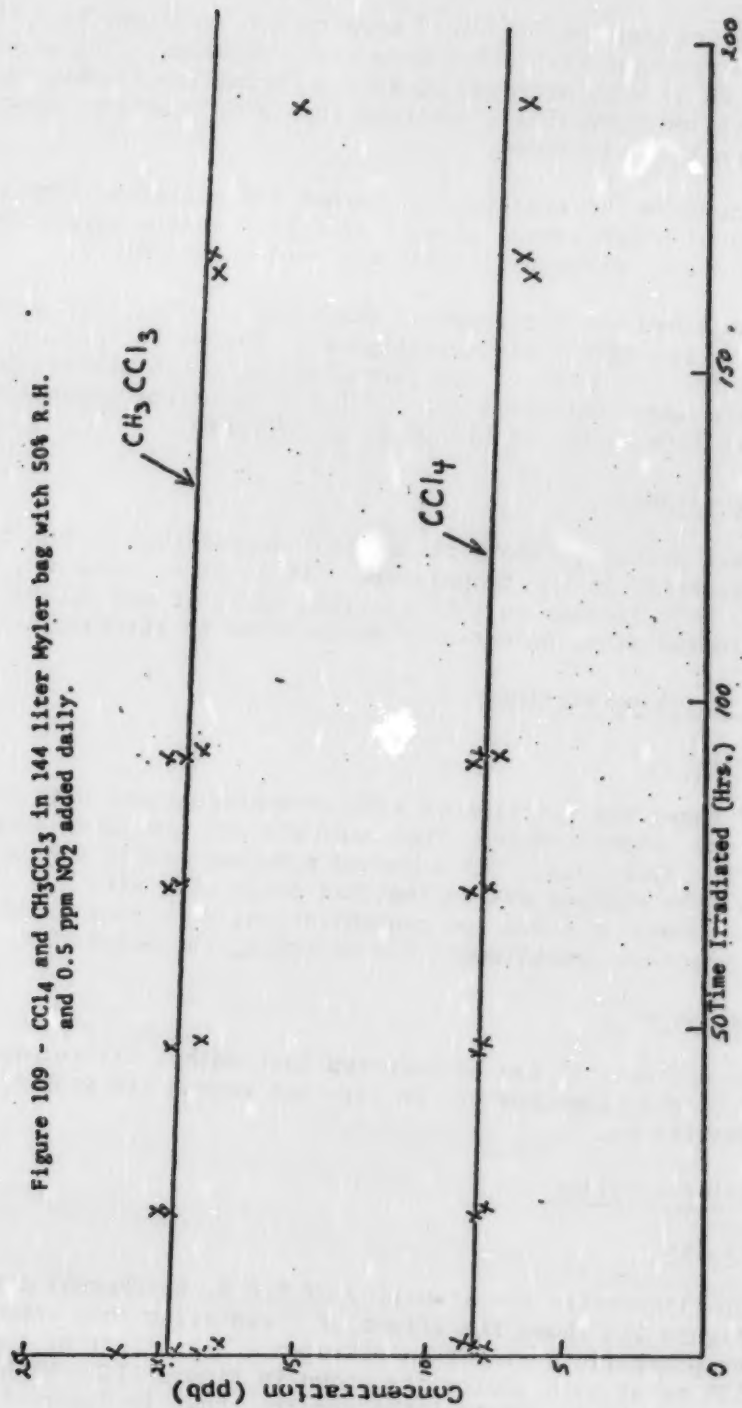


Figure 110
TRICHLOROETHYLENE + O₃
dark reaction

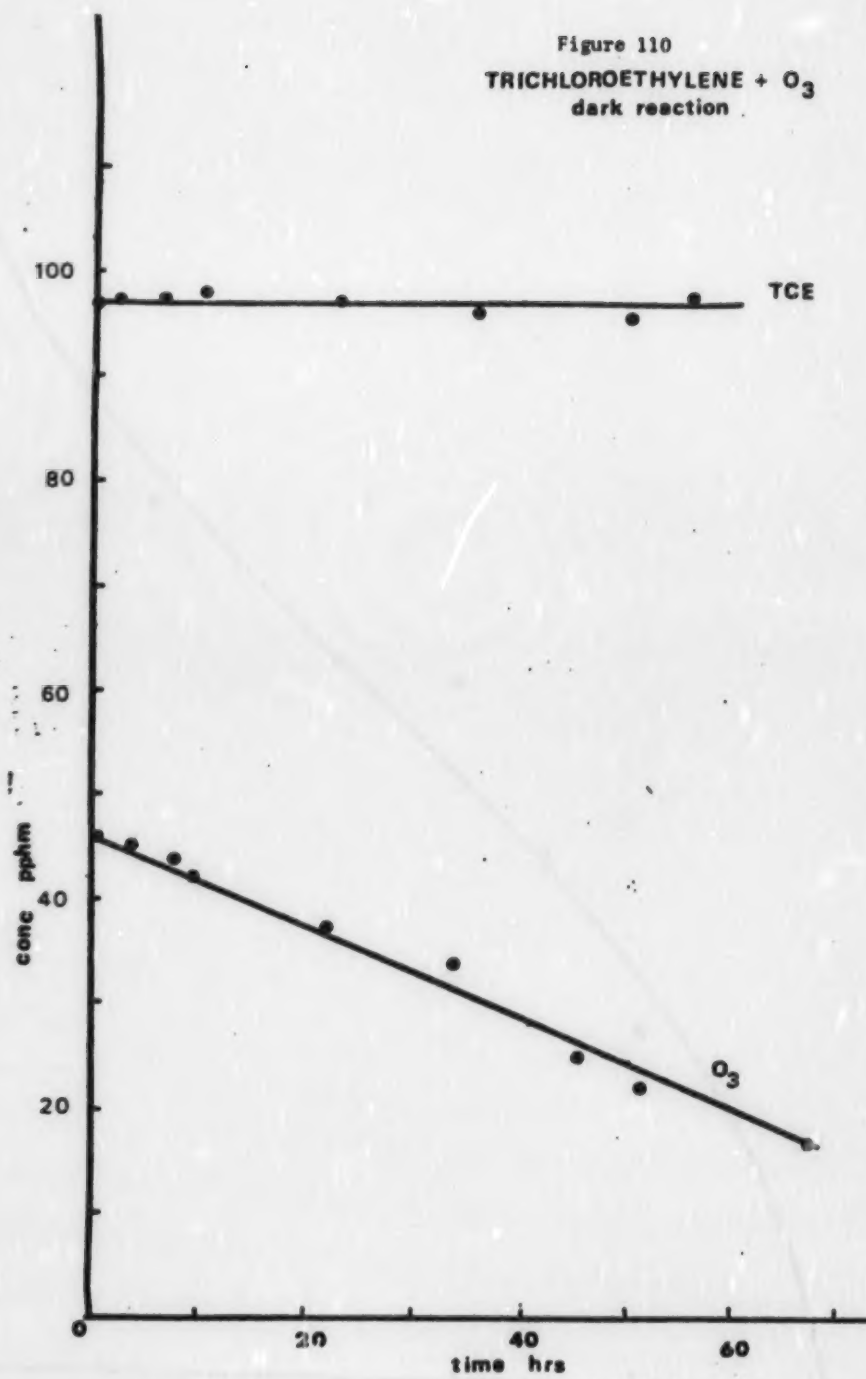


Figure 111 - Trichloroethylene in N_2 irradiated in a 200 liter teflon bag

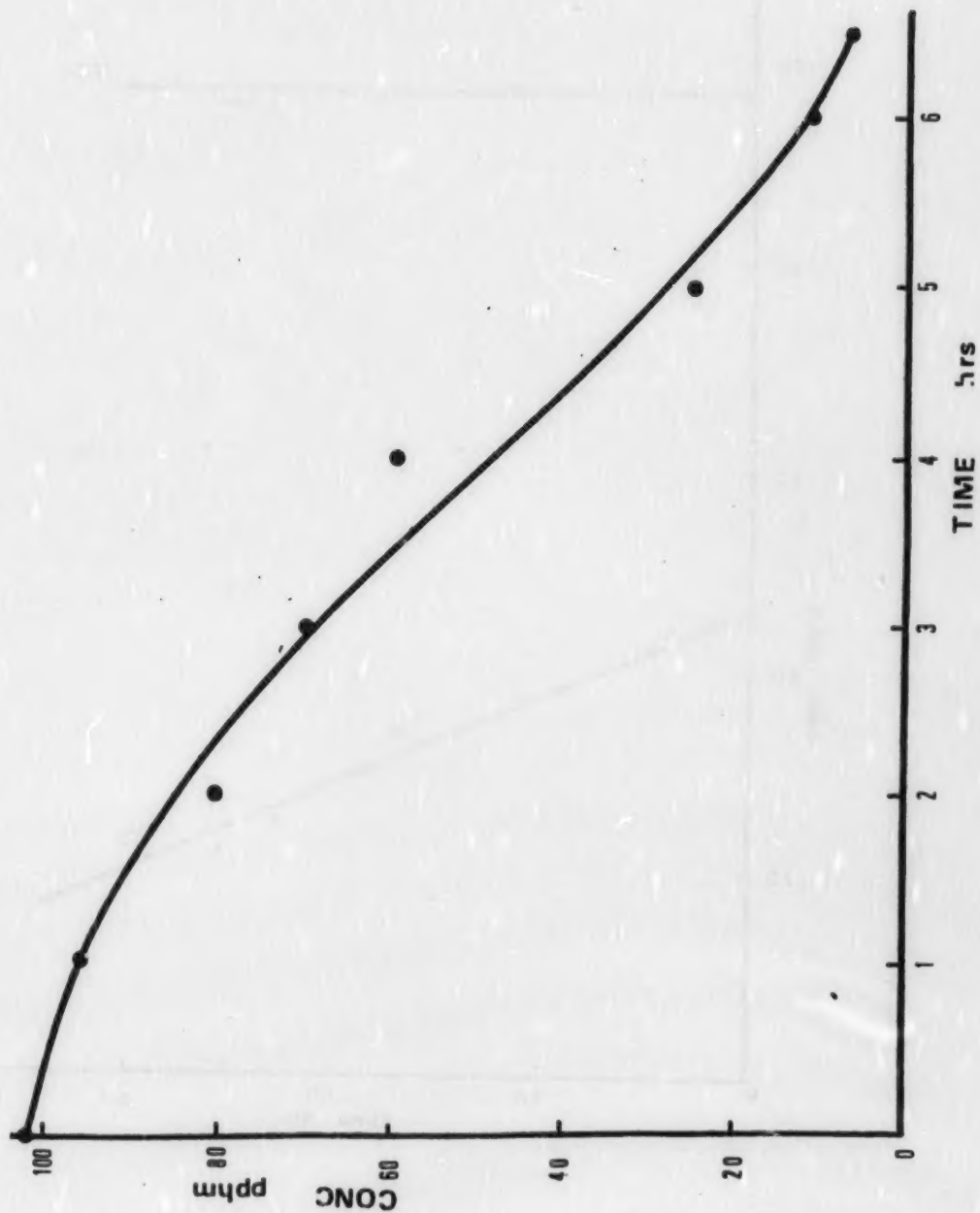
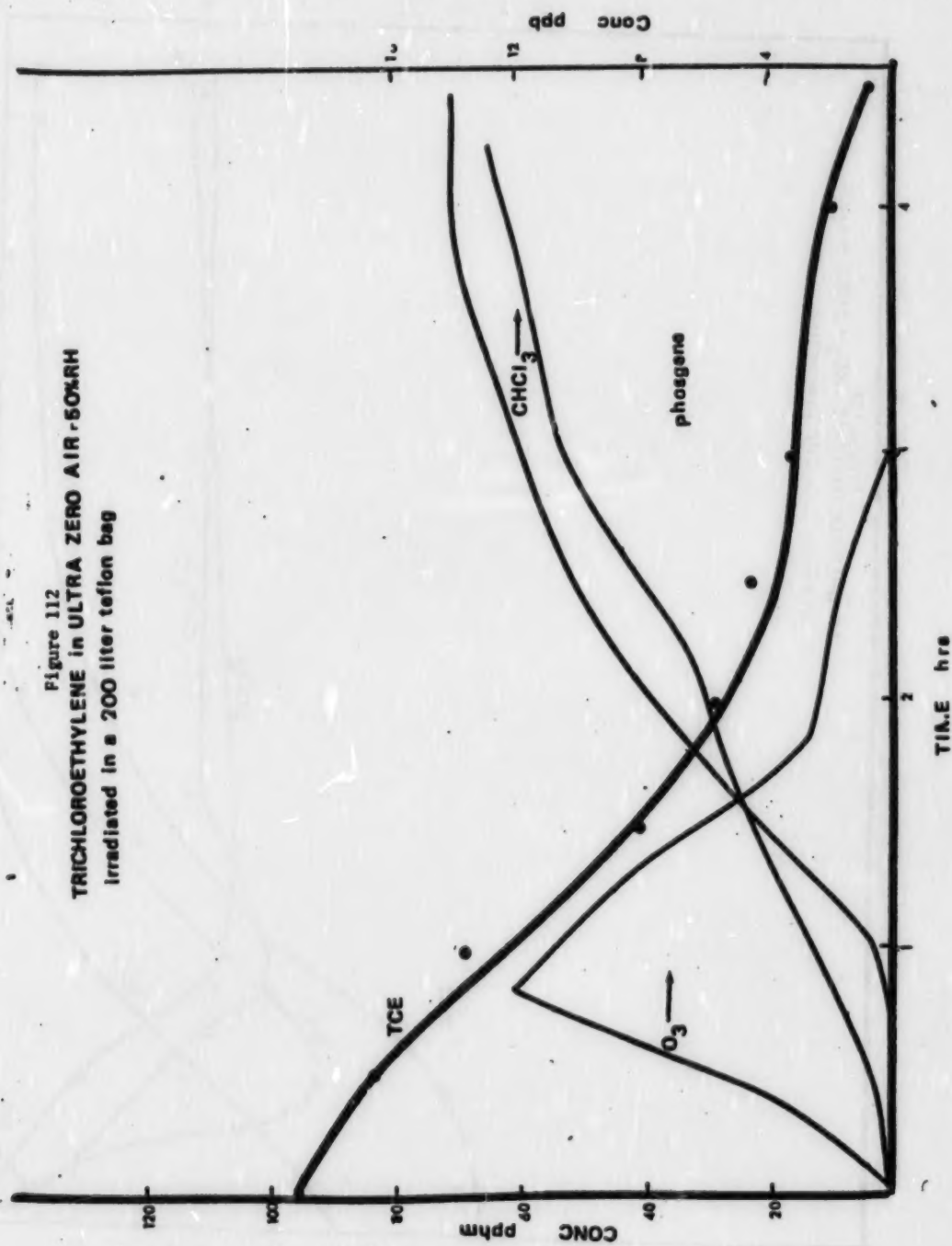


Figure 112
 TRICHLOROETHYLENE in ULTRA ZERO AIR-50XRH
 Irradiated in a 200 liter teflon bag



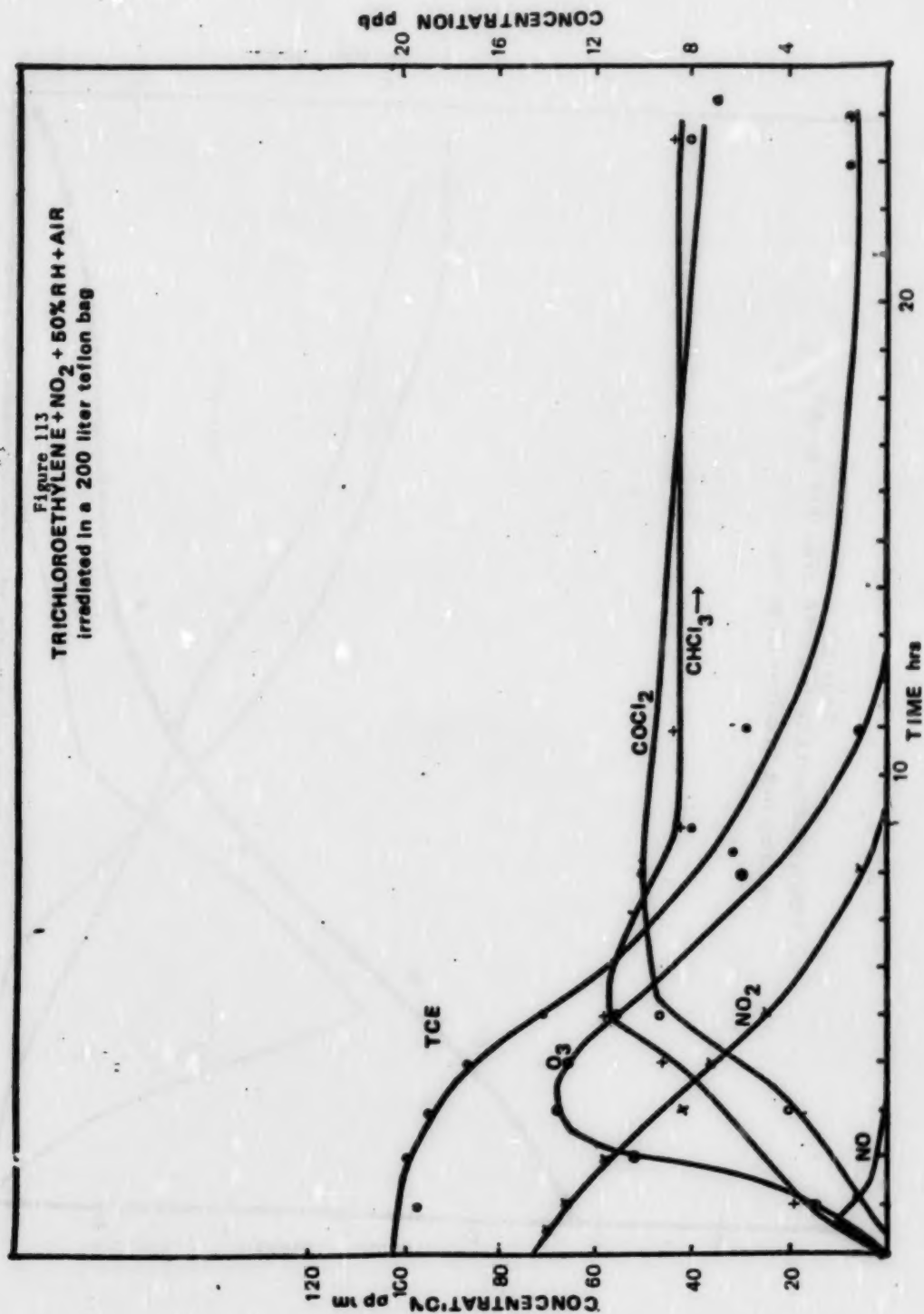
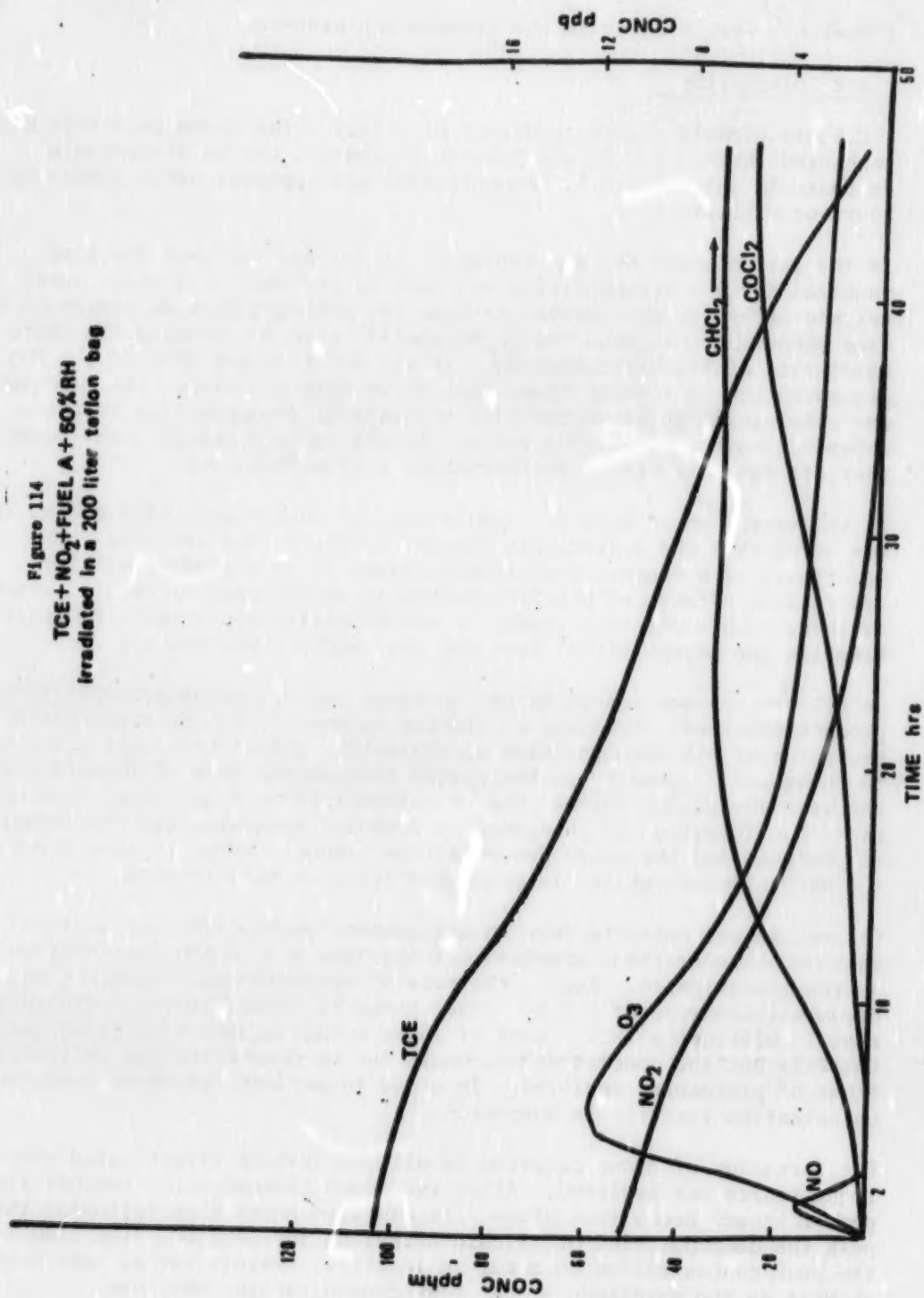


Figure 114
TCE + NO₂ + FUEL A + 50% RH
Irradiated in a 200 liter teflon bag



("Fuel A") were present in the irradiation mixture.

7.6.2 Discussion -

T.C.E. is clearly stable to direct O₃ attack - the ozone half-life was unchanged whether T.C.E. was present or absent, and no discernable decrease in initial T.C.E. concentration was apparent after almost 60 hours of exposure to O₃.

In the system where NO₂ was employed, it was noticed that the time required for 95% decomposition was much longer than in systems where trichloroethylene was reacted without the nitrogen dioxide present. This same phenomenon was observed by Wilson⁽²¹⁾ when she studied the photoreactivity of trichloroethylene. It was noted by her that if the NO₂ concentration is several times that of trichloroethylene, the reaction was completely inhibited and that the rate of decomposition is quite dependent on the T.C.E./NO₂ ratio. As the ratio decreased, she noted that all the measures of photoreactivity also decreased.

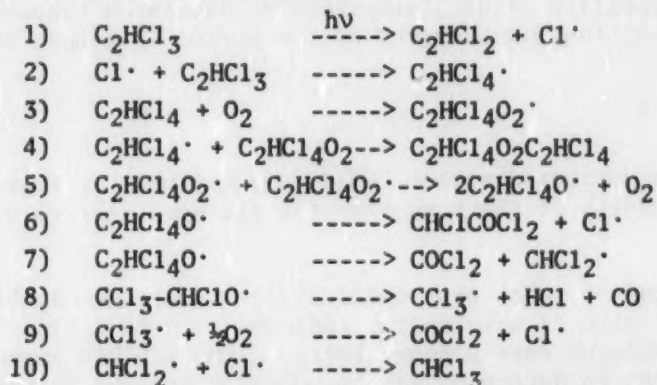
In the system where both nitrogen oxide and Fuel A were introduced, it was noted that the hydrocarbon further inhibited the reaction. The occurrence of a competitive reaction seems to be a good possibility. The synergistic effects of one hydrocarbon to another are extremely hard to evaluate, and since this report is not primarily concerned with reaction kinetics the possibilities were not thoroughly investigated.

In all the systems investigated, phosgene was the major decomposition product observed. By doing a chlorine balance it can be seen that at the point of 95% decomposition approximately 30% of the budget is converted to phosgene. Depending on the system studied the rate of formation of phosgene varied; the quicker the trichloroethylene dissociated, the more rapid the formation of phosgene. A proposed mechanism for the formation of phosgene and the other decomposition products which is consistent with the present observations is presented later in this section.

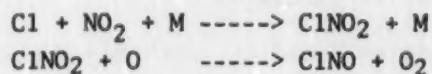
Chloroform was noted to form in all systems where light was employed, the maximum concentrations observed varying from 8 - 15 ppb depending on the system investigated. Again, the rate of formation was dependent on the decomposition rate of T.C.E. Other products identified were dichloroacetyl chloride and HCl. Both of these products were identified qualitatively but the concentrations could not be quantified due to limitations of procedures employed. In order to account for these products a chlorination reaction is suspected.

The formation of ozone occurred in all the systems investigated where a light source was employed. After the ozone concentration reached its peak a steady decay took place. It was also noted that following the peak the decomposition of trichloroethylene accelerated. The time for the peak concentration to occur in identical systems varied considerably as well as the magnitude of the peak concentrations observed.

The following reaction mechanism is proposed in order to account for the observed formation of the products mentioned. The mechanism involves a chlorine-sensitized photo-oxidation of trichloroethylene. Huybrechts et al. (75) did work on the chlorine photosensitized oxidation of trichloroethylene but in their case Cl_2 was added as a primary reactant. The mechanism they proposed was discussed earlier in this report. This mechanism could not account for the results observed in this study but some of the reactions are included. The proposed mechanism for the present study is as follows:



This mechanism accounts for the products and the time lags observed in the various systems investigated. Time is required for the initial propagation of chlorine radicals, oxygen radicals and radical-radical species. The time lag varied significantly from one system to another due to the presence of NO_2 and fuel competing for the radicals being formed. The time lag in the systems with nitrogen dioxide is substantially longer than in the systems not incorporating NO_2 . This is suspected to be due to nitrogen dioxide competing for $\text{Cl}^\cdot$ radical thereby increasing the time required for trichloroethylene decomposition and product formation. Evidence to this occurring is provided when the chlorine budgets in runs incorporating NO_2 and those not incorporating NO_2 are compared. The products observed in the runs not incorporating NO_2 account for approximately 41% of the chlorine initially present, where in the systems with NO_2 added the products observed only account for about 24% of the chlorine. A possible competitive reaction follows:



If this reaction occurs it can account for the differences in the chlorine budgets. Further evidence of this competition occurring is provided by Figures 113 and 114. These figures demonstrate that as the NO_2 concentration drops off the inhibition becomes less severe and the trichloroethylene decomposes at a much more rapid rate. Similarly, the mechanism can account for the increased time lag when Fuel A is added to the system. In this case again a competition for free radicals is expected. The reactive

olefin species provided by the hydrocarbon competes with the trichloroethylene for the $C_2HCl_4^{\cdot}$ species as well as the $Cl^{\cdot}$ chain carrier. Once the olefinic species is reacted, then the photo-dissociation of trichloroethylene proceeds at a much more rapid rate.

7.7 Ethylene Dichloride

7.7.1 Results -

Figure 115 shows the stability of dichloroethane to simulated tropospheric conditions. No decomposition was observed over a period of almost 400 hours.

7.7.2 Discussion -

Ethylene dichloride is a saturated alkane, held together only by sigma bonds. Extremely high energy of short wavelengths are necessary to promote the electrons.

In order for any compound to react photochemically, it must be capable of absorbing light in the range of wavelengths employed. In this study the wavelengths of light employed were predominantly in the visible region of the spectra. In order to determine if the compound absorbs in the region the spectrum covering the UV and visible portions was examined, and it was found that it was transparent to wavelengths greater than 2900Å. Therefore, light present in the chamber or in the troposphere could not cause the compound to react.

It is also evident from Figure 115 that dichloroethylene is also very unreactive towards reactive photochemical intermediates. Tropospheric reactions are thus unlikely to be a major sink for the compound.

7.8 Vinyl chloride

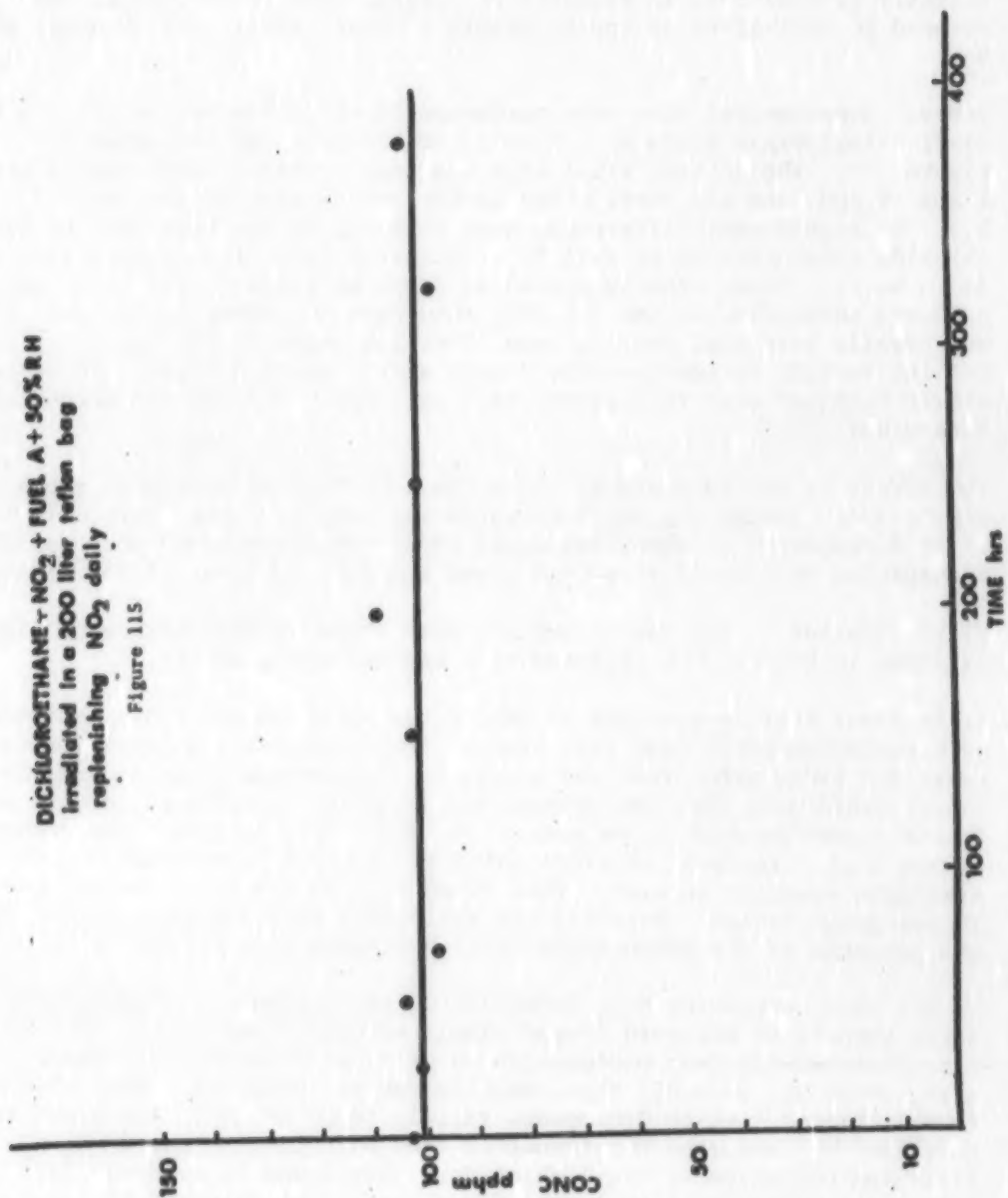
All experiments were performed using 200 liter Teflon bags filled as previously described (Section 4.2.4). Vinyl chloride initially at $\approx 1 - 10$ ppm was irradiated with simulated sunlight under the following conditions:

- a) in ultra zero air at 50% relative humidity
- b) in dry nitrogen
- c) in ultra zero air at 50% relative humidity, with NO_2 present, initially at 0.2 to 6 ppm
- d) as for (c), with hydrocarbon present.

The dark reaction between vinyl chloride and ozone (~ 5 ppm) in ultra zero air at 50% relative humidity was also studied.

7.8.1 Results and Discussion -

The effects of irradiating vinyl chloride in air at 50% relative humidity



are shown in Figure 116. For comparative purposes the corresponding data for a nitrogen atmosphere are also shown. It can be seen that in both cases the removal of vinyl chloride is rather slow, with only a slightly greater rate in presence of oxygen. The removal rates correspond to half-lives of approximately 17 hours in air and 30 hours in N_2 .

Several experimental runs were performed in which NO_2 was present in the vinyl chloride/air mixtures. Results of one such run are shown in Figure 117. The initial vinyl chloride concentrations were varied between 1 and 10 ppm, and the vinyl chloride: NO_2 ratios were in the range 1.4 to 5.3. No significant differences were observed in the time for the vinyl chloride concentration to fall by a factor of two - the average time was 3 ± 0.6 hours. Ozone usually peaked at about this time. The other reaction products identified in the V.C./ NO_2 runs were NO, formaldehyde and HCl. NO was usually very low, peaking soon after the start of the irradiation, and falling rapidly to undetectable levels within about 3 hours. Formaldehyde slowly built up over this period to 1 or 2 ppm. HCl was not quantitatively determined.

The effect of adding hydrocarbon to the V.C./ NO_2 /air system is shown in Figure 118. Though the NO_2 /V.C. ratio was very low, the vinyl chloride still disappeared at about the usual rate. NO disappeared very rapidly, accompanied by a rapid rise in O_3 , and a steady build-up of formaldehyde.

Vinyl chloride in air reacts rapidly with ozone in the absence of light, as shown in Figure 119. Formaldehyde and HCl are products.

It is clear that in presence of NO_2 , O_3 or hydrocarbon, vinyl chloride is more photochemically reactive, than in their absence. In experiments where the hydrocarbon fuel was added, NO disappearance was especially rapid, confirming that the hydrocarbon supplies significant amounts of reactive species such as radicals. We might have expected that hydrocarbon would also protect vinyl chloride by itself competing for the available reactive species. This evidently did not occur in our systems to any great extent. Possibly the additional radicals made available by the presence of the hydrocarbon counterbalanced this effect.

In all runs containing NO_2 , formaldehyde was a product. Approximately equal amounts of HCl were formed simultaneously. Gay et al.⁽⁷⁸⁾ have also observed HCl from photooxidation of vinyl chloride. In their work, about 50% more HCl than formaldehyde was produced. They also report formyl chloride, which decomposes rapidly to CO and HCl. Sanhueza and Heicklen⁽⁹⁹⁾ observed HCl formation from both Cl-atom and $O(^3P)$ -initiated oxidation of vinyl chloride. They found no evidence for formyl chloride formation in the former case, but observed it, as well as CO, HCl and formic acid, in the latter case. Apparently HCl is both a primary and a secondary product.

The major product observed in our experiments was ozone. The peak O_3 values correlated strongly with the initial levels of NO_2 present. When

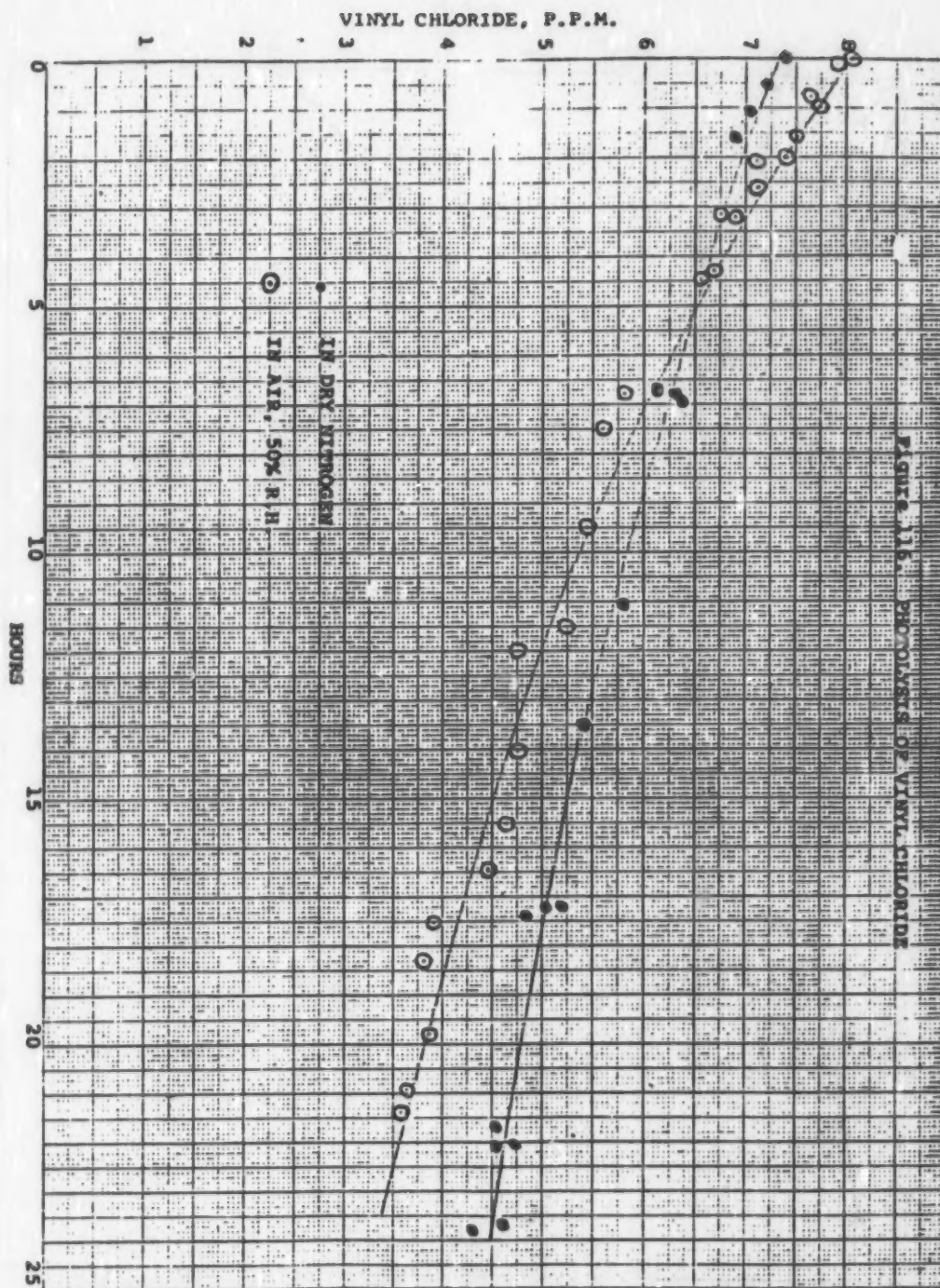
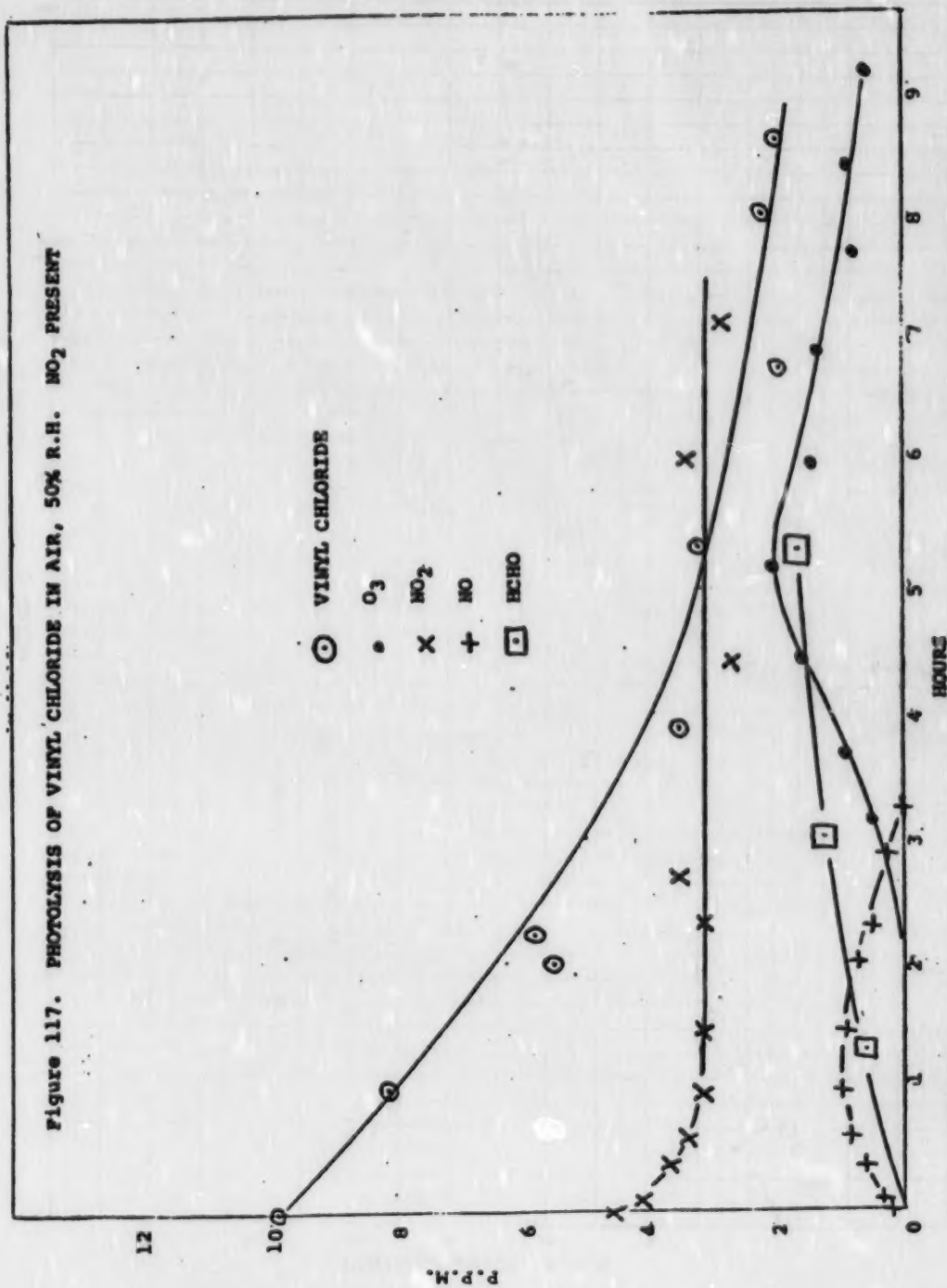
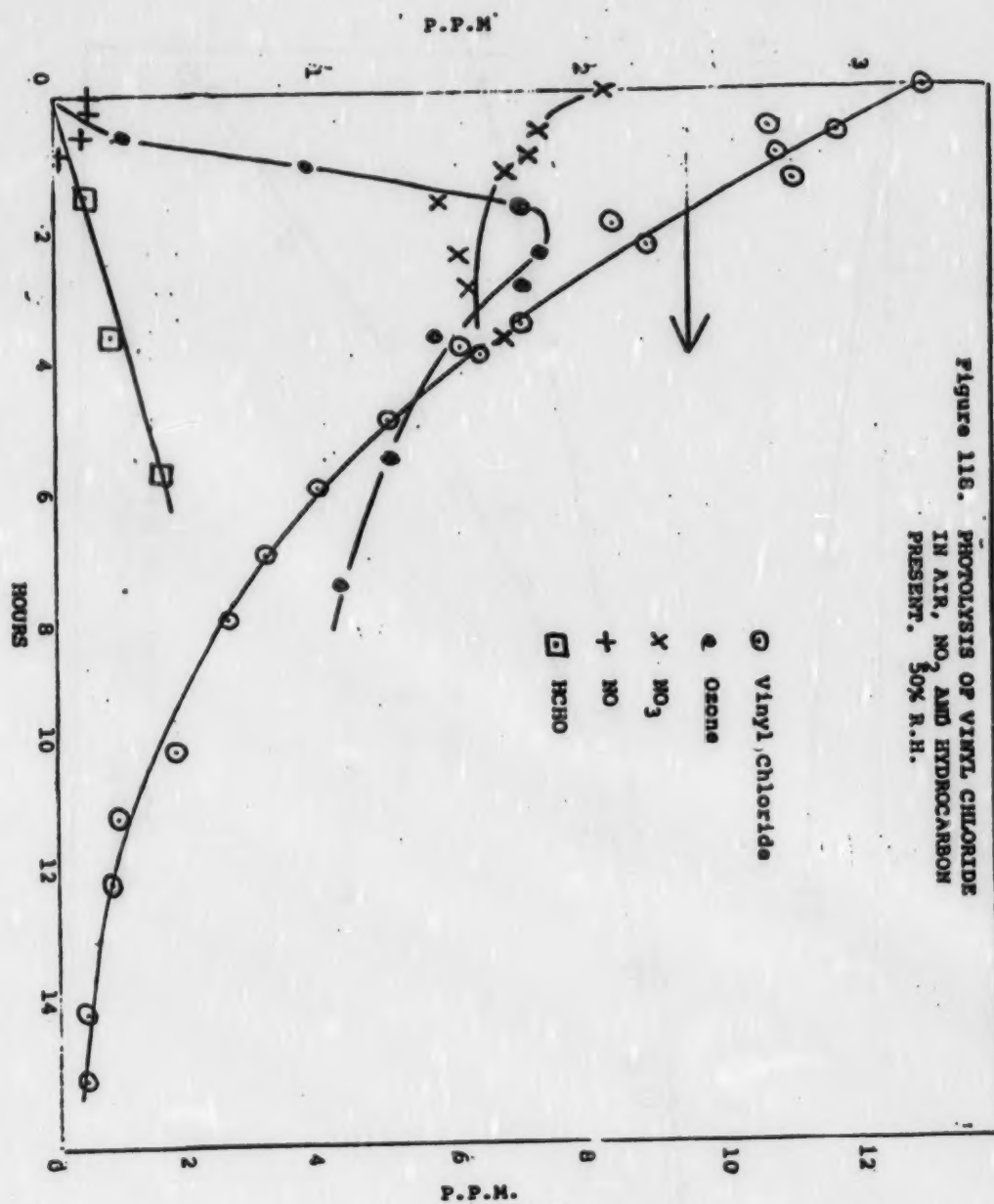
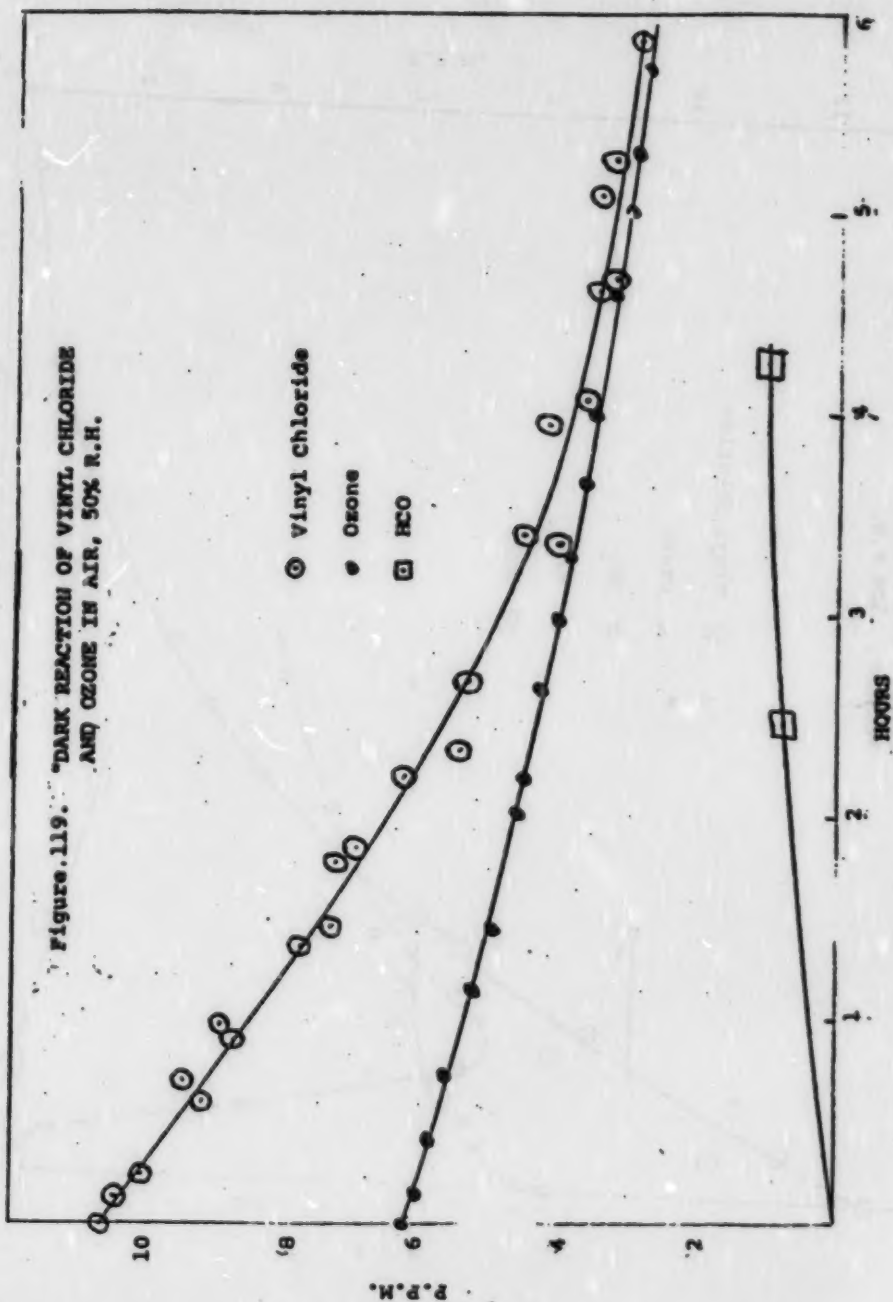


Figure 117. PHOTOLYSIS OF VINYL CHLORIDE IN AIR, 50% R.H. NO₂ PRESENT







hydrocarbon was present, initial ozone production was particularly rapid, peaking in about 2 hours, as compared with 3-5 hours for runs where hydrocarbon was absent. This is as expected, as O_3 build-up is partly due to the oxidation of NO to NO_2 by organic radicals, followed by NO_2 photolysis. Ozone attack on vinyl chloride is certainly a major factor in the removal of V.C. in our experiments, as may be seen by the "dark" reaction (Figure 119). Possibly an intermediate cyclic ozonide is formed, which can break up into either formyl chloride, CO and H_2O or formaldehyde, CO_2 and HCl. The low levels of HCl observed, however, imply that other halogenated reaction products, not measured in this study must also be formed.

Vinyl chloride would appear to be quite reactive photochemically in presence of NO_2 and hydrocarbons, and would presumably be fully photodecomposed in the troposphere, though near emission sources it might persist under adverse meteorological conditions.

7.9 Dichloromethane

Simulated tropospheric irradiation for up to 16 hours of dichloromethane in various mixtures in nitrogen, ultra-zero air, NO_2 and hydrocarbon fuel resulted in no significant decrease in dichloromethane concentration. This compound is evidently quite stable under these conditions. This finding agrees with those of others, such as Dilling et al. (116), McConnell et al. (196) and Wilson and Doyle (197).

7.10 PCB's

The following laboratory investigation was designed: (a) to simulate some important physical and chemical parameters characteristic of both clean air and polluted air and (b) to study the effect of those parameters on the rates of disappearance and products formed of a selected chlorinated biphenyl.

Commercially prepared mixtures of PCB's as mentioned previously are complex mixtures of between 50 and 100 isomers. The use of these mixtures in photochemical studies poses a nightmare in analyses and interpretation of product formation. Therefore, we deemed it advantageous to study a selected isomer. It was estimated that the results of such a study would yield mechanistically interpretable products.

Ortho-chlorobiphenyl (OCB) was chosen since: (a) it is present in commercial PCB formulations, (b) it is volatile and (c) it exhibits an ultraviolet absorption similar to other PCB isomers (Figure 3). From a practical standpoint, the isomer could be obtained from commercial sources in a very pure form (Analabs, Inc., North Haven, Connecticut).

7.10.1 Results and Discussion -

All experiments were performed in 250 liter FEP Teflon bags, the details of which have been described (Section 4.1.1). All experiments employed

50% relative humidity conditions.

Stability of OCB in the Absence of Ultraviolet Radiation - As indicated by Figure 120 less than 12% of OCB is lost from the gas phase over a 24 hour period. The 250 liter sample of 1.7 ppm OCB declined to 1.5 ppm in the absence of ultraviolet radiation. This was found to represent an unacceptable loss in the light of the experimental design.

Effect of Ultraviolet Wavelength Intensity on Rate of OCB Destruction - Since OCB absorbs ultraviolet radiation coincident with incident tropospheric radiation, the effect of variation in intensity of those wavelengths on OCB was studied in an "inert" atmosphere. Irradiations were carried out in nitrogen at 50% relative humidity. This was considered as an inert photochemical environment since neither N_2 or H_2O absorb energy in the range utilized. In addition, both require energies greater than could be supplied by any energy transfer processes to rupture their bonds⁽⁴²⁾. Traces of oxygen present (primarily permeation through Teflon film) will weakly absorb some long wavelengths (in the visible range) but represent little potential to effect chemical change in OCB. The bond energies of N_2 , H_2O , and O_2 are 226, 119 and 117 Real/mole respectively which are higher than the highest energy found in the simulated tropospheric ultraviolet radiation utilized (~99 Real/mole). However, the carbon-chlorine bond, which possesses a strength of 58-97 Real/mole depending on the carbon's other bonds, does have the potential to rupture under these conditions. The other bonds in the biphenyl structure are of energy beyond the tropospheric cut off.

The first experiment utilized radiation which roughly represents the quality of the tropospheric ultraviolet spectrum. It is difficult to determine the absolute intensity of this range without elaborate and expensive instrumentation.

The result of these runs are displayed graphically in Figures 121 and 122 respectively as concentration and log concentration OCB as a function of irradiation time. A 59% loss of the starting concentration was observed.

The second experiment involved changing the spectral distribution of the incident radiation. By increasing the lamp distribution from 6 to 24 sun-lamps, the intensity of the 310 nanometer band is effectively quadrupled since the blacklamps do not remit in this range.

The results of three runs are displayed graphically in Figures 123 and 124 respectively as concentration and log concentration OCB as a function of irradiation time. A 97% loss of the starting concentration was observed.

If it is assumed that OCB absorbs radiation in the 310 nanometer range resulting in chemical change,

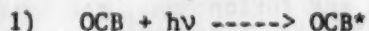


FIGURE 120

ORTHO-CHLOROBIPHENYL STABILITY IN 250 LITER TEFLON BAGS
IN THE ABSENCE OF ULTRAVIOLET RADIATION.

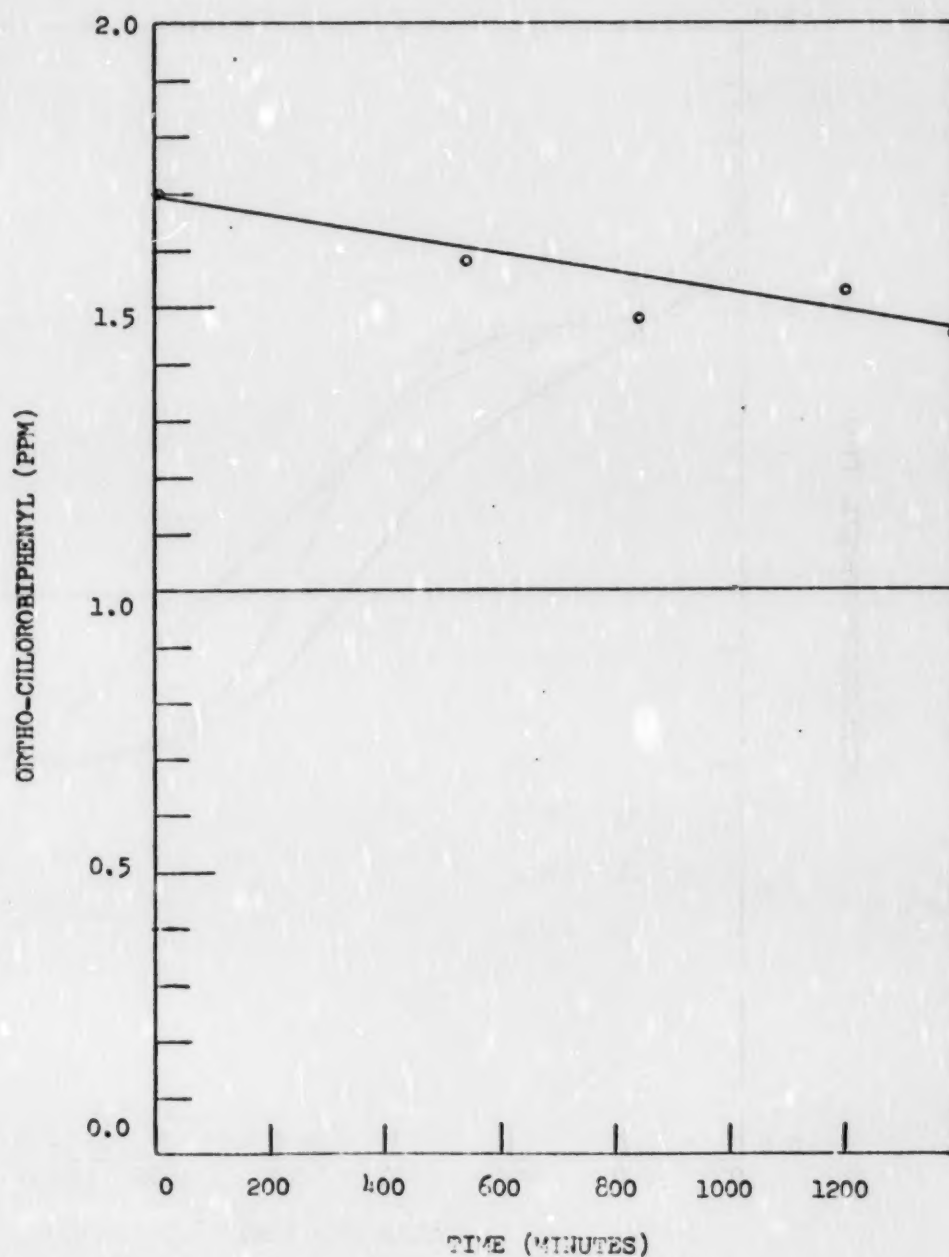


FIGURE 121

ORTHO-CHLOROBIPHENYL IN NITROGEN IRRADIATED WITH
SIMULATED TROPOSPHERIC RADIATION (LINEAR PLOT).

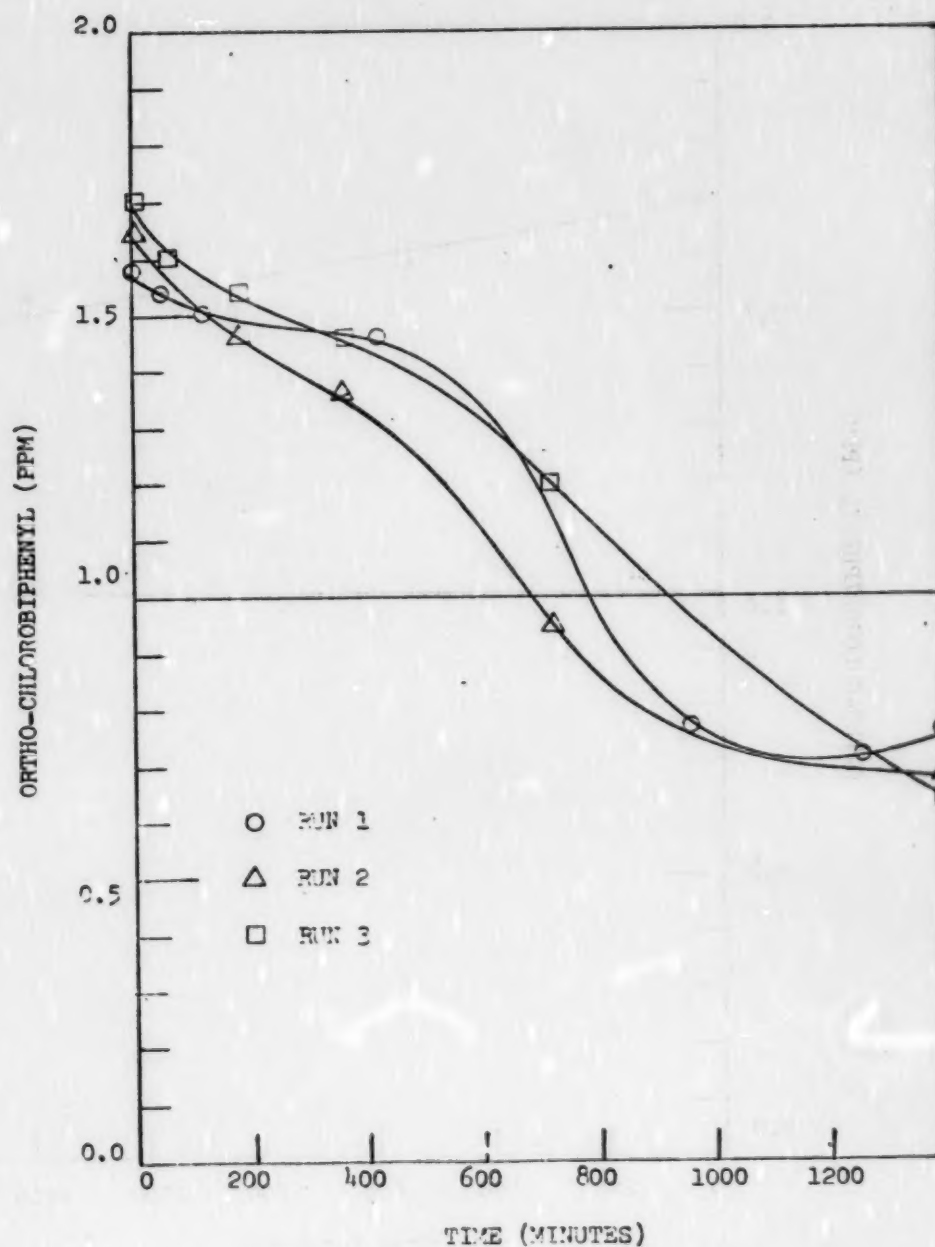


FIGURE 122

ORTHO-CHLOROBIPHENYL IN NITROGEN IRRADIATED WITH SIMULATED
TROPOSPHERIC RADIATION (LOG CONCENTRATION VS. TIME).

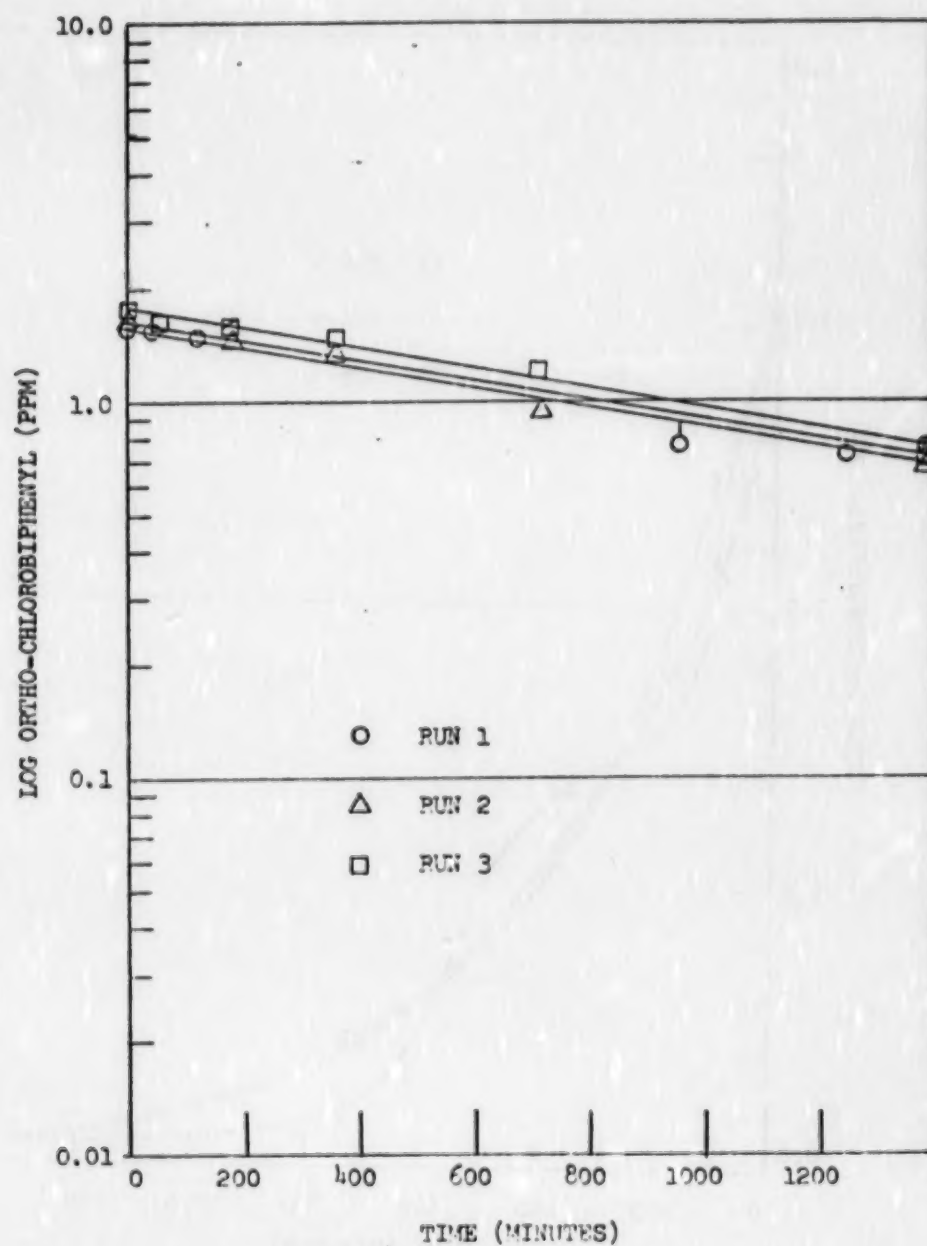


FIGURE 123

ORTHO-CHLOROBIPHENYL IN NITROGEN IRRADIATED WITH FOURFOLD
310 NANOMETER INTENSITY SOURCE (LINEAR PLOT).

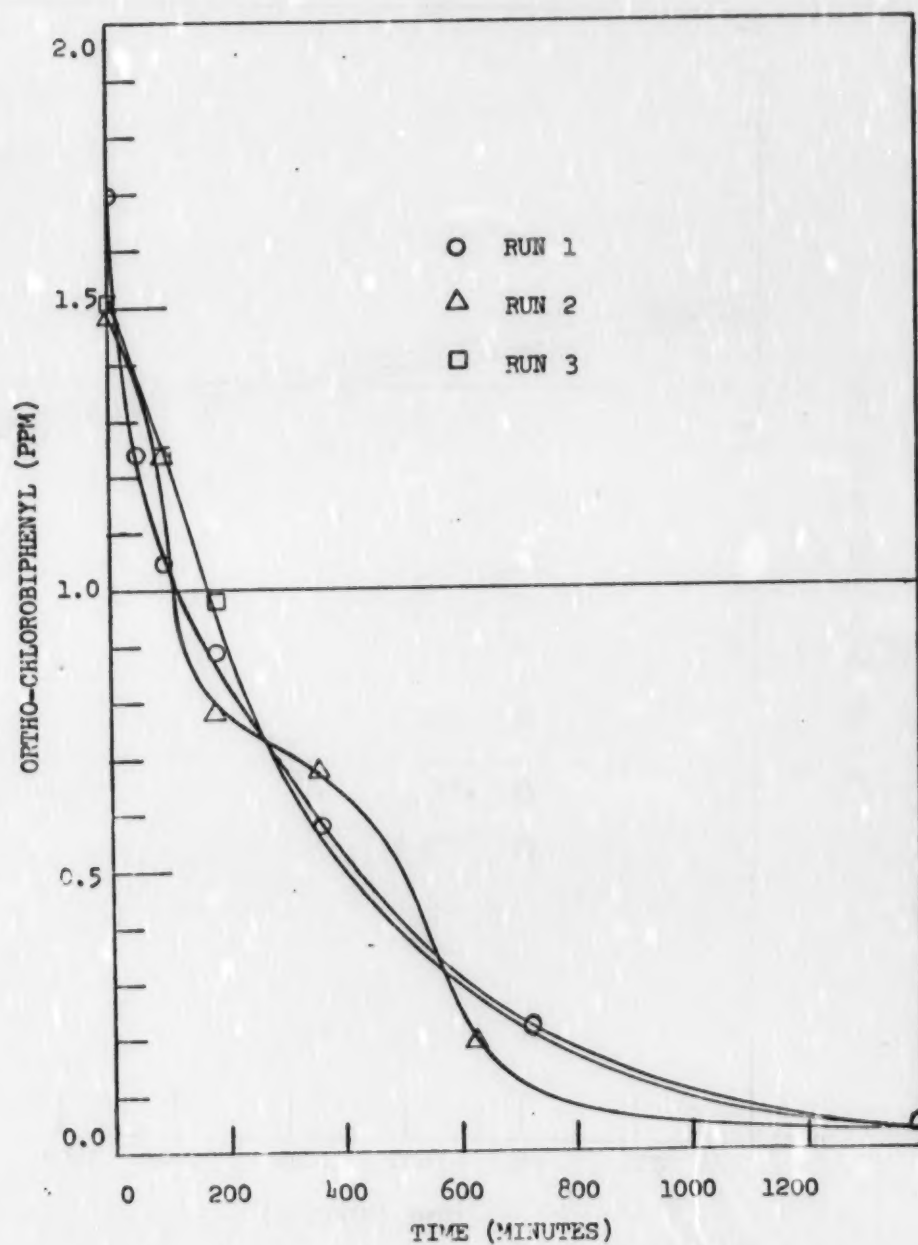
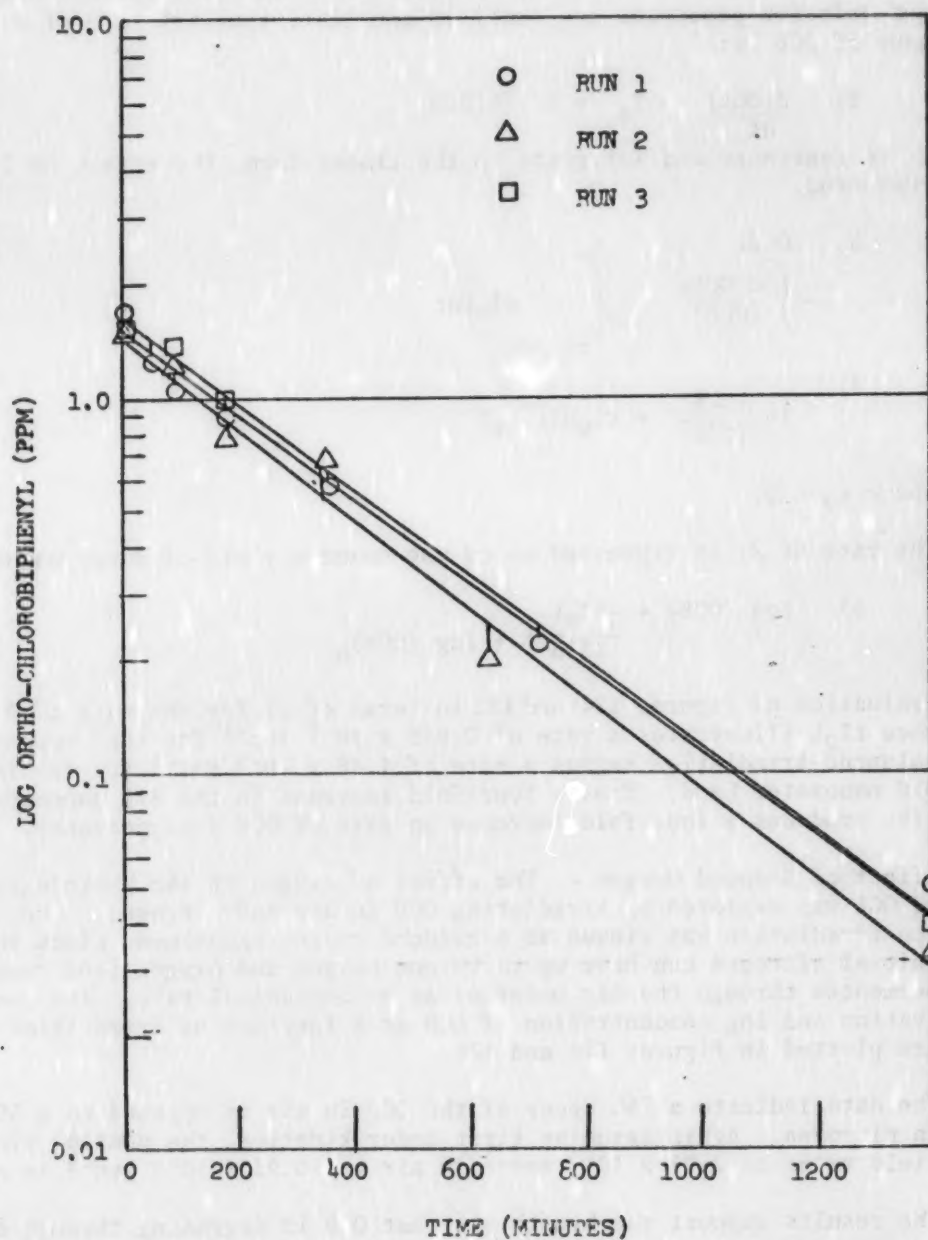


FIGURE 124

ORTHO-CHLOROBIPHENYL IN NITROGEN IRRADIATED WITH FOURFOLD
310 NANOMETER INTENSITY SOURCE (LOG CONCENTRATION VS. TIME).



the rate of disappearance of OCB is expressed as I_a the rate of absorption of OCB. I_a is equal to the product of the molar extinction coefficient ϵ , the integrated light intensity I , the pathlength L , and the concentration of OCB. The rate of disappearance of OCB is hence, dependent on the concentration of excited OCB*.

If it is assumed that the rate of absorption assuming thermal deactivation and emission processes are small or constant, then the rate of disappearance of OCB is:

$$2) \quad \frac{d(\text{OCB})}{dt} = I_a = \epsilon I (L(\text{OCB}))$$

if we rearrange and integrate to the linear form, the effect of I can be evaluated.

$$3) \quad \text{OCB}_t - \int_{\text{OCB}_0}^{\text{OCB}_t} \frac{d(\text{OCB})}{(\text{OCB})} = \int_{t_0}^t \epsilon I_0 L dt$$

$$4) \quad \ln \frac{(\text{OCB})_0}{(\text{OCB})} = \epsilon I_0 h(t-t_0)$$

where $t_0 = 0$.

The rate of 2) is expressed as ϕ_d the quantum yield of disappearance.

$$5) \quad \log (\text{OCB}) = \frac{-t I_0 L}{2.303} + \log (\text{OCB})_0$$

Evaluation of Figures 124 and 122 in terms of 5) for the rate of disappearance $\epsilon I_0 L$ illustrates a rate of $0.948 \times 10^{-5} \text{ sec}^{-1}$ for the tropospherically balanced irradiation versus a rate of $4.48 \times 10^{-5} \text{ sec}^{-1}$ for the increased 310 nanometer band. Thus a four-fold increase in the 310 nanometer intensity produces a four-fold increase in rate of OCB disappearance.

Effect of Reduced Oxygen - The effect of oxygen in the photodegradation of OCB was explored by irradiating OCB in air and nitrogen. The nitrogen irradiation was viewed as a reduced oxygen experiment since the initial nitrogen can have up to 20 ppm oxygen and oxygen from room air permeates through the bag material at a substantial rate. The concentration and log concentration of OCB as a function of irradiation time are plotted in Figures 125 and 126.

The data indicate a 75% decay of the OCB in air as opposed to a 59% decay in nitrogen. Again assuming first order kinetics, the semilog plots yield rates of $2.01 \times 10^{-5} \text{ sec}^{-1}$ in air vs. $0.95 \times 10^{-5} \text{ sec}^{-1}$ in nitrogen.

The results support the hypothesis that OCB is degrading through direct

FIGURE 125

ORTHO-CHLOROBIPHENYL IN AIR IRRADIATED WITH SIMULATED
TROPOSPHERIC RADIATION (LINEAR PLOT).

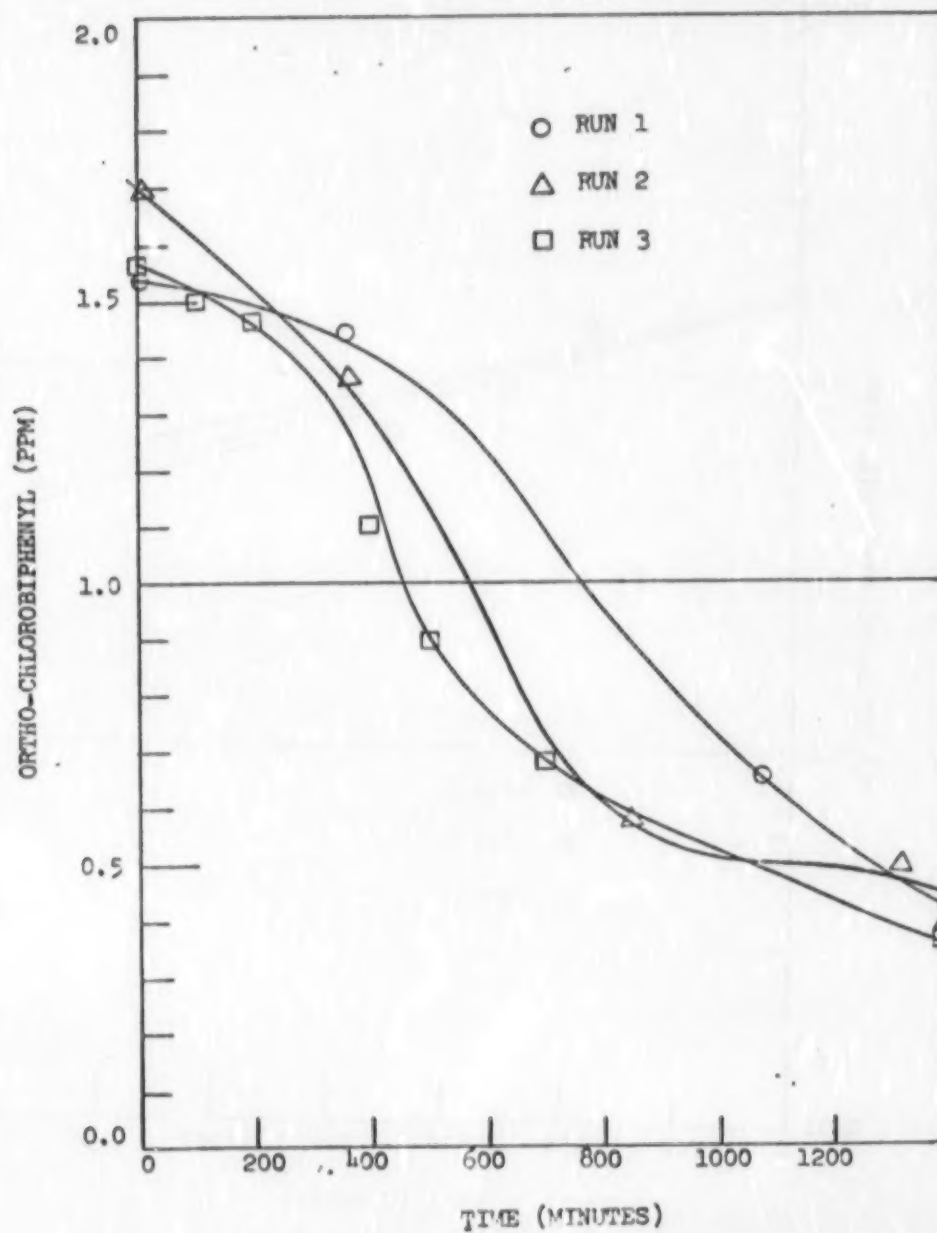
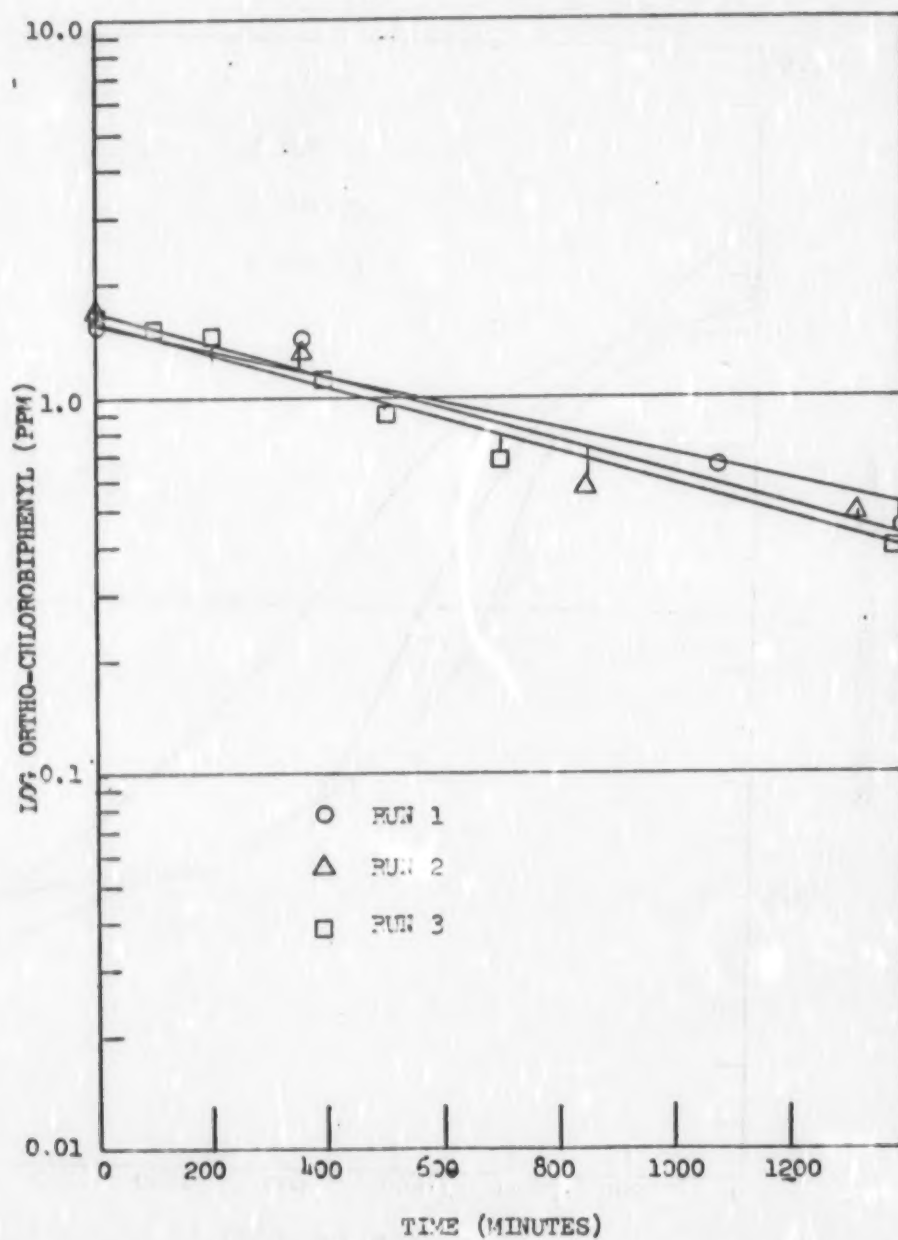


FIGURE 126

ORTHO-CHLOROBIPHENYL IN AIR IRRADIATED WITH SIMULATED
TROPOSPHERIC RADIATION (LOG CONCENTRATION VS. TIME).



photodissociation. The slower rate of decay in nitrogen is expected since the unreactive nitrogen functions as a collisional deactivating body for the excited OCB*. Collisional deactivation returns the electronically excited OCB* to its undissociated ground state before photodissociation can occur.

Oxygen also can function as collisional energy absorber. However, the photodissociated OCB would probably react readily with molecular oxygen. Thus, in air the biphenyl radical reacts with oxygen to form a peroxybiphenyl radical. In the nitrogen environment the lack of reactive oxygen also makes more likely the recombination of the biphenyl radical and atomic chlorines thus producing the observed slower rate of decay.

Chlorinated Products - On the assumption that atomic chlorine is generated upon the rupture of the weak carbon-chlorine bond, it is believed that the photodissociated chlorine produces hydrogen chloride under tropospheric conditions. Wofsy and McElroy in a tropospheric/stratospheric model calculated that kinetic and thermodynamic considerations favor the formation of HCl in the troposphere⁽¹⁹⁸⁾. Chlorine dioxide (ClO₂), which is probably formed readily from the reaction of free chlorine and the abundant molecular oxygen, readily photodissociates under tropospheric conditions. Other species less likely formed considering the unlikely reaction of two chlorine atoms are chlorine monoxide (Cl₂O) and free chlorine (Cl₂). These would also be readily photodissociated under tropospheric conditions^(178, 199). Hydrogen chloride, however, will be readily formed in the presence of molecular or atomic hydrogen. Hydrogen chloride will not dissociate under the influence of tropospheric radiation and is stable in the chemical dynamics of troposphere⁽¹⁹⁸⁾. In the real troposphere HCl probably reacts with ammonia to form ammonium chloride. However, in the purified air used, it was assumed that ammonia was not present (<10 ppb based on NO_x measurements) and therefore the chlorine was analyzed as soluble chloride ion (Cl⁻) along with hydrogen ion (H⁺).

Figures 127, 128 and 129 illustrate the corporation of H⁺ and Cl⁻ concentrations (expressed as micrograms M³) as a function of irradiation time. Perhaps more revealing is the production of H⁺ and Cl⁻ normalized against the OCB lost. Assuming that all OCB lost forms equimolar concentrations of HCl then a plot of the data should show a constant ratio (product observed to product calculated from OCB loss) of 1.0. Figures 130, 131 and 132 illustrate the results for the chlorine yields. Figures 133, 134 and 135 similarly demonstrate the corresponding hydrogen ion yield.

Although a constant 1.0 ratio was not obtained, a few observations are in order. The scatter observed in the earlier part of the irradiations is in general much greater than the final data points. This is not unexpected since the precision of the potentiometric method at low ion concentrations is poor. Additionally, changes in OCB concentration at high concentrations are more difficult to detect due to the non-linearity of the electron capture detector.

FIGURE 127

SOLUBLE CHLORIDE AND HYDROGEN ION PRODUCTION IN THE
NITROGEN/FOURFOLD 310 NANOMETER INTENSITY IRRADIATION (LOG
CONCENTRATION VS. TIME).

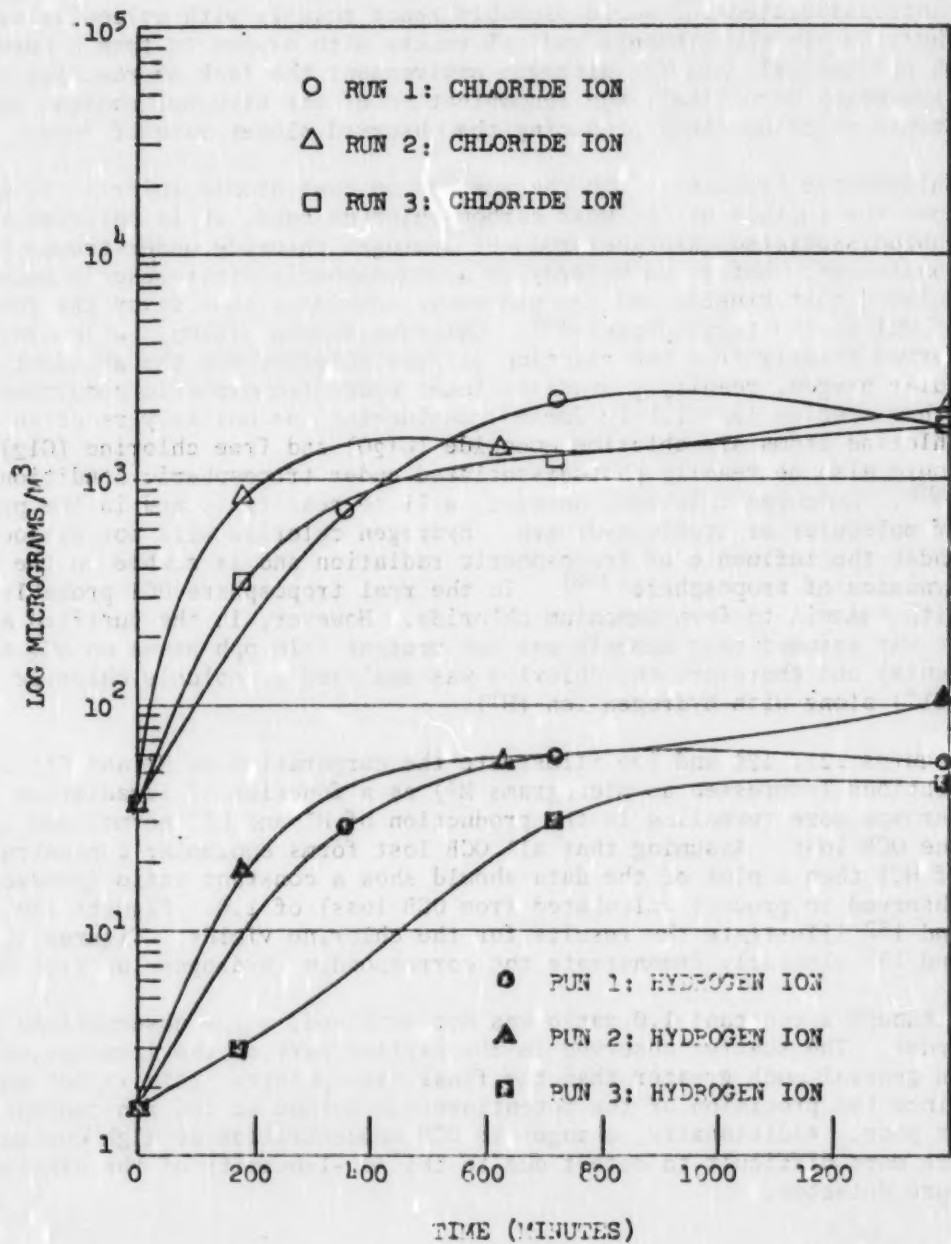


FIGURE 128

SOLUBLE CHLORIDE AND HYDROGEN ION PRODUCTION IN THE
NITROGEN/SIMULATED TROPOSPHERIC IRRADIATION (LOG CONCENTRATION
VS. TIME).

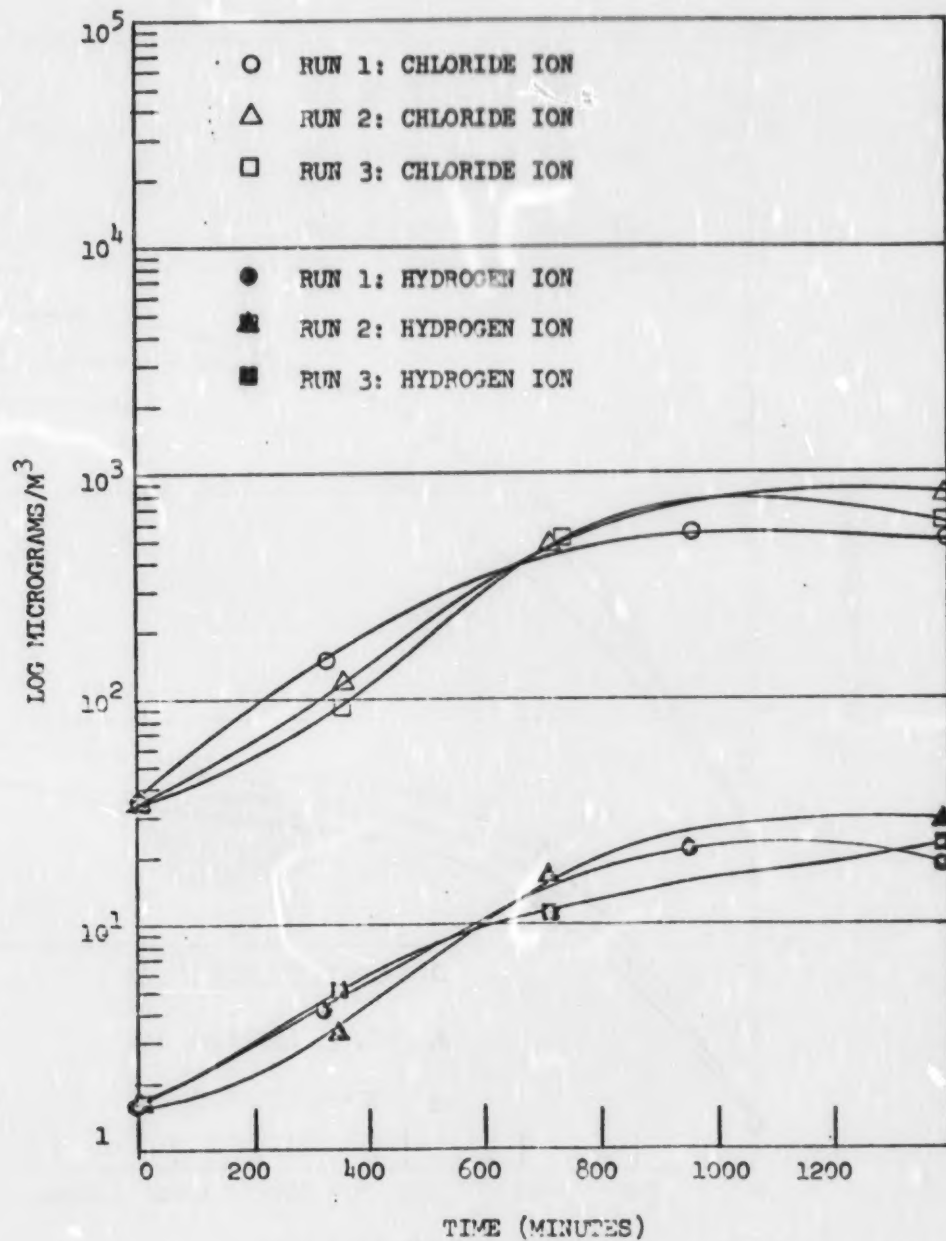


FIGURE 129

SOLUBLE CHLORIDE AND HYDROGEN ION PRODUCTION IN THE AIR/
SIMULATED TROPOSPHERIC IRRADIATION (LOG CONCENTRATION VS. TIME).

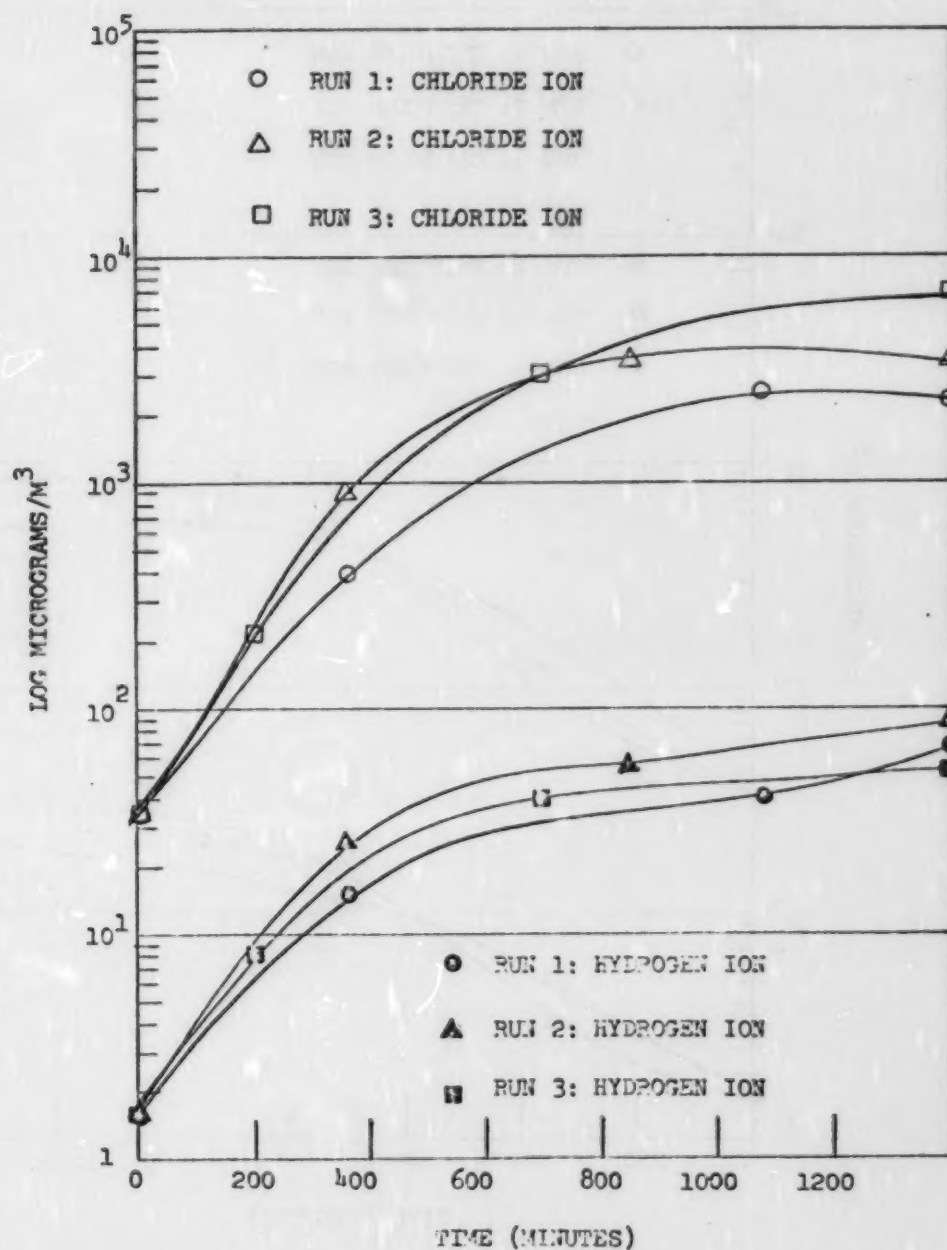


FIGURE 130

CHLORIDE ION:ORTHO-CHLOROBIPHENYL LOSS VS. TIME IN THE
NITROGEN/FOURFOLD 310 NANOMETER INTENSITY IRRADIATION.

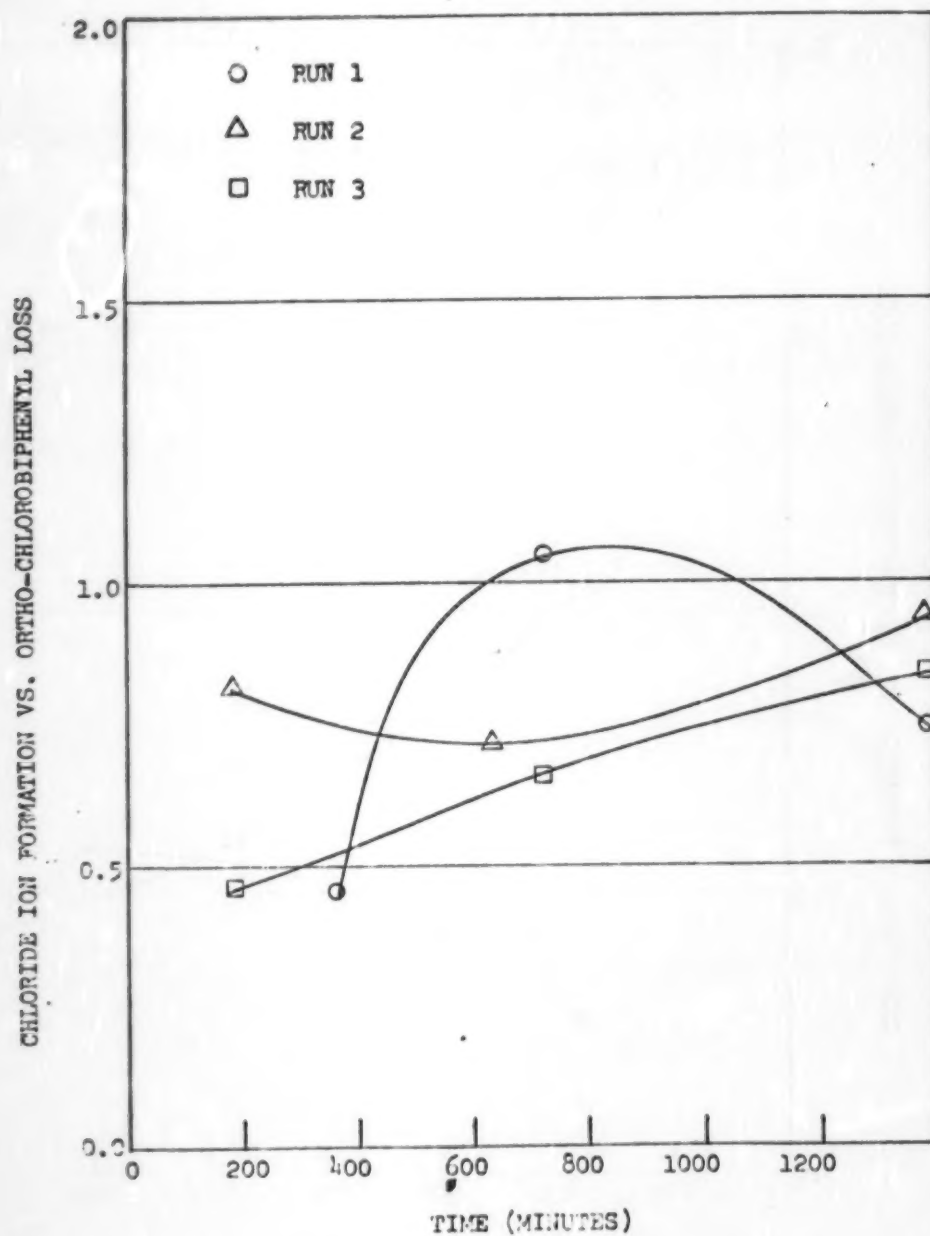


FIGURE 131

CHLORIDE ION:ORTHO-CHLOROBIPHENYL LOSS VS. TIME IN THE
NITROGEN/SIMULATED TROPOSPHERIC IRRADIATION.

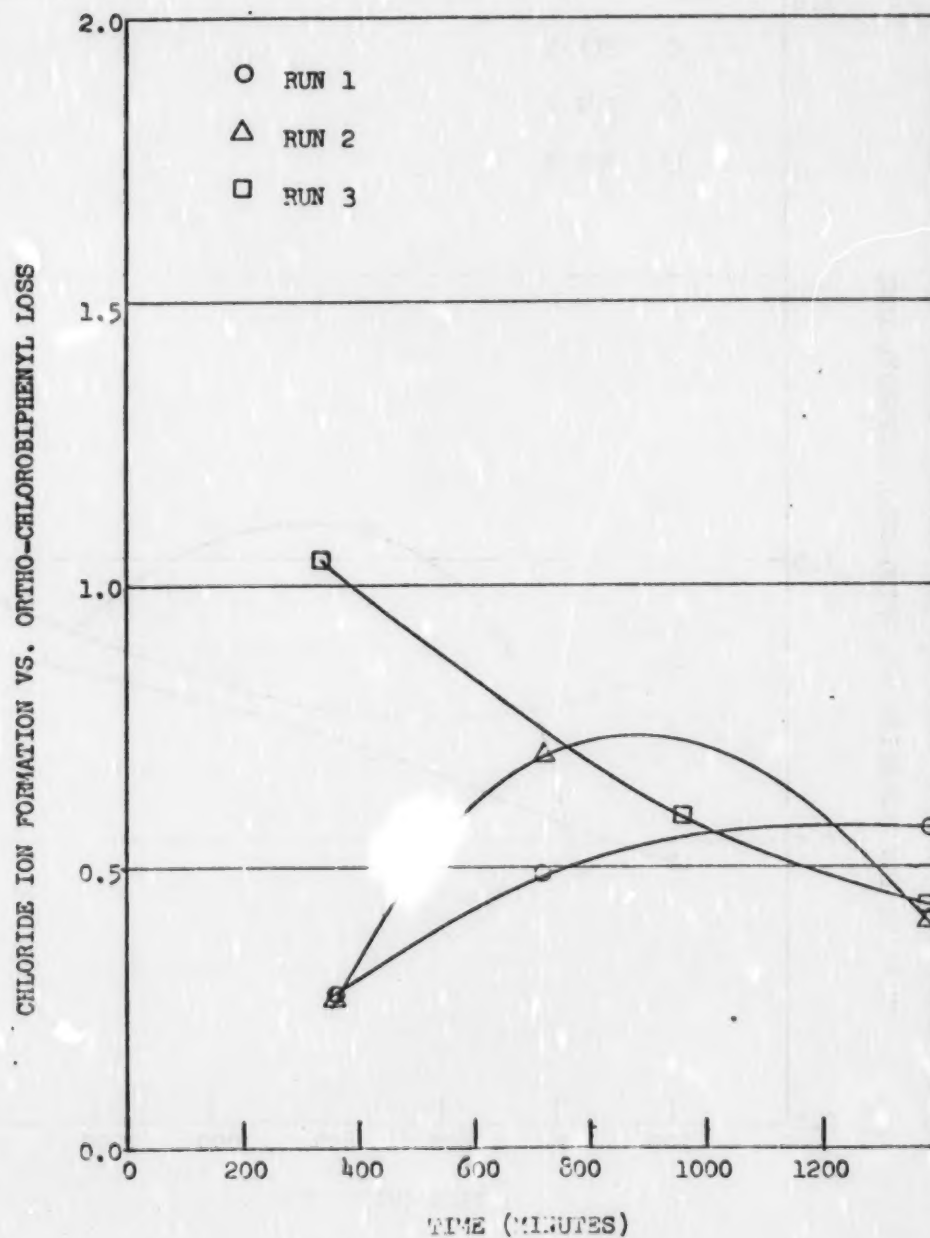


FIGURE 132

CHLORIDE ION:ORTHO-CHLOROBIPHENYL LOSS VS. TIME IN THE AIR/
SIMULATED TROPOSPHERIC IRRADIATION.

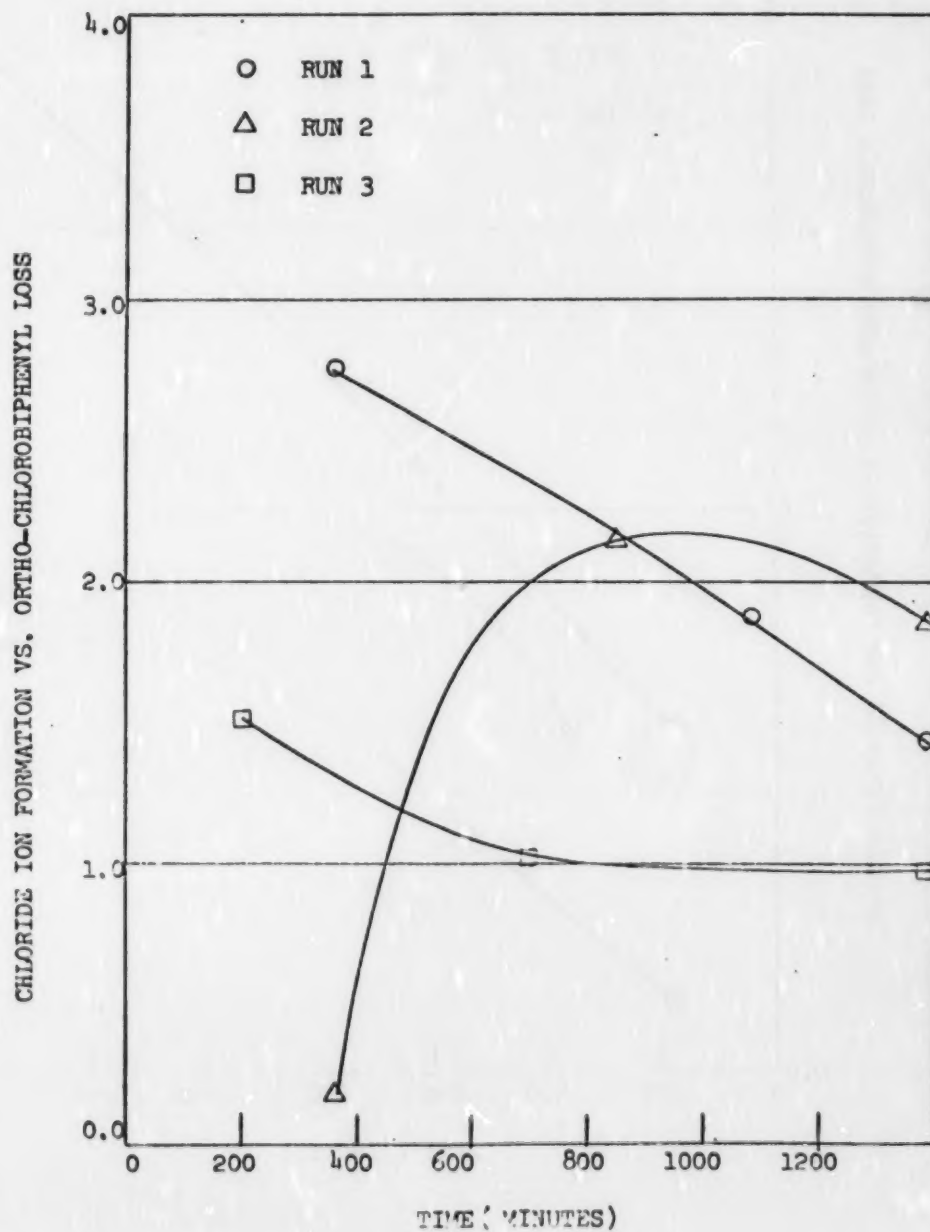


FIGURE 133

SOLUBLE HYDROGEN ION FORMATION: ORTHO-CHLOROBIPHENYL LOSS
VS. TIME IN THE NITROGEN/FOURFOLD 310 NANOMETER INTENSITY IRRADIATION.

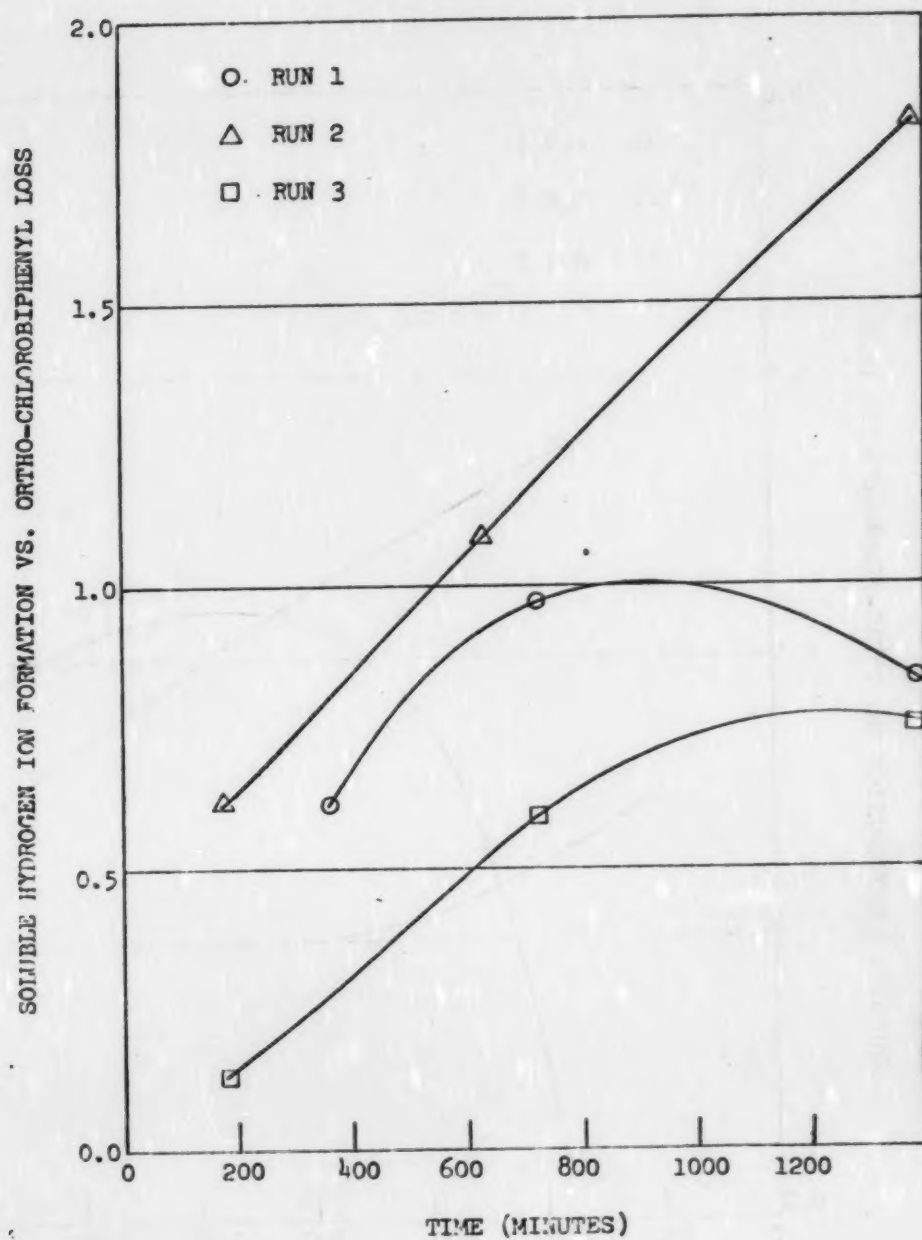


FIGURE 134

SOLUBLE HYDROGEN ION:ORTHO-CHLOROBIPHENYL LOSS VS. TIME IN
NITROGEN/SIMULATED TROPOSPHERIC IRRADIATION.

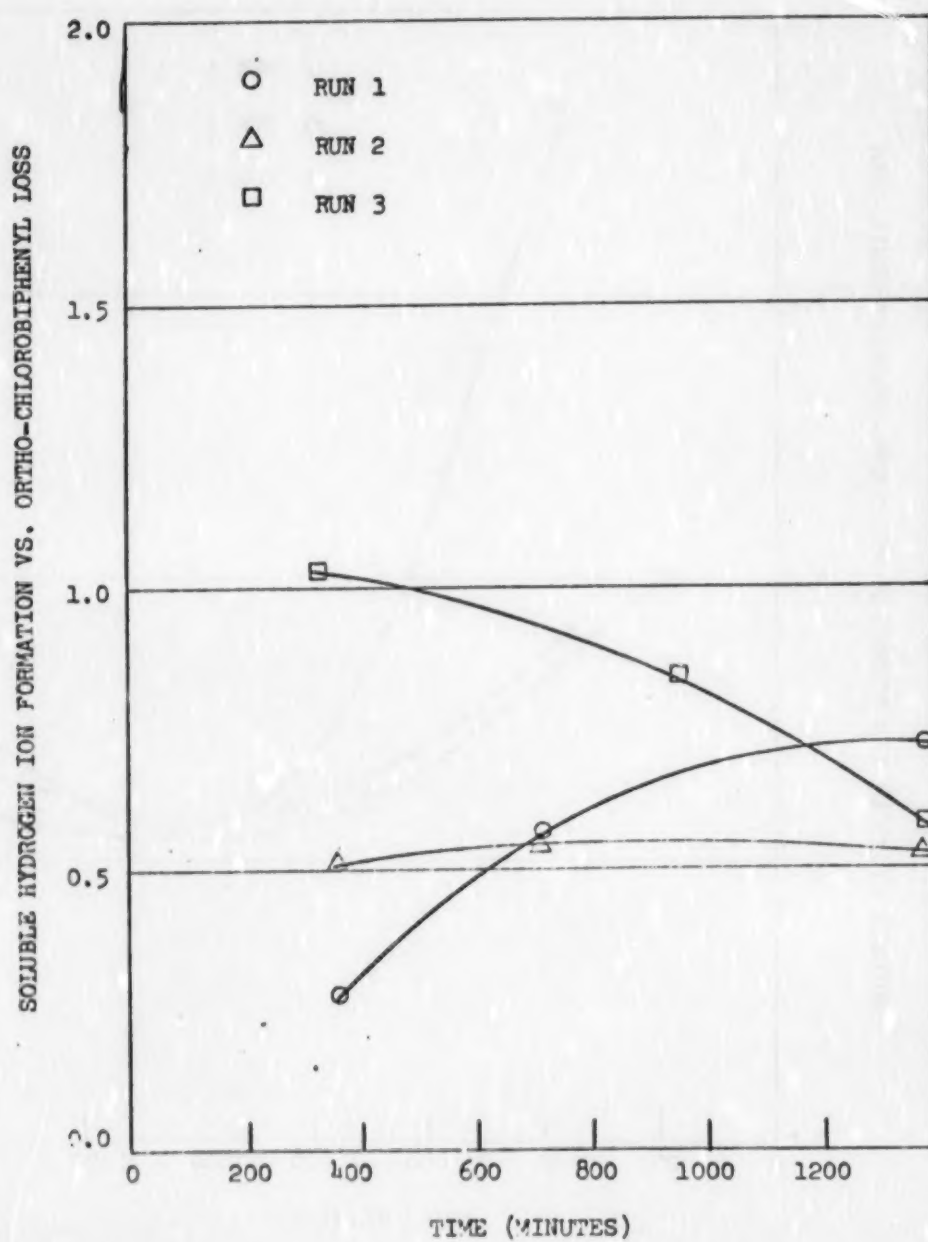
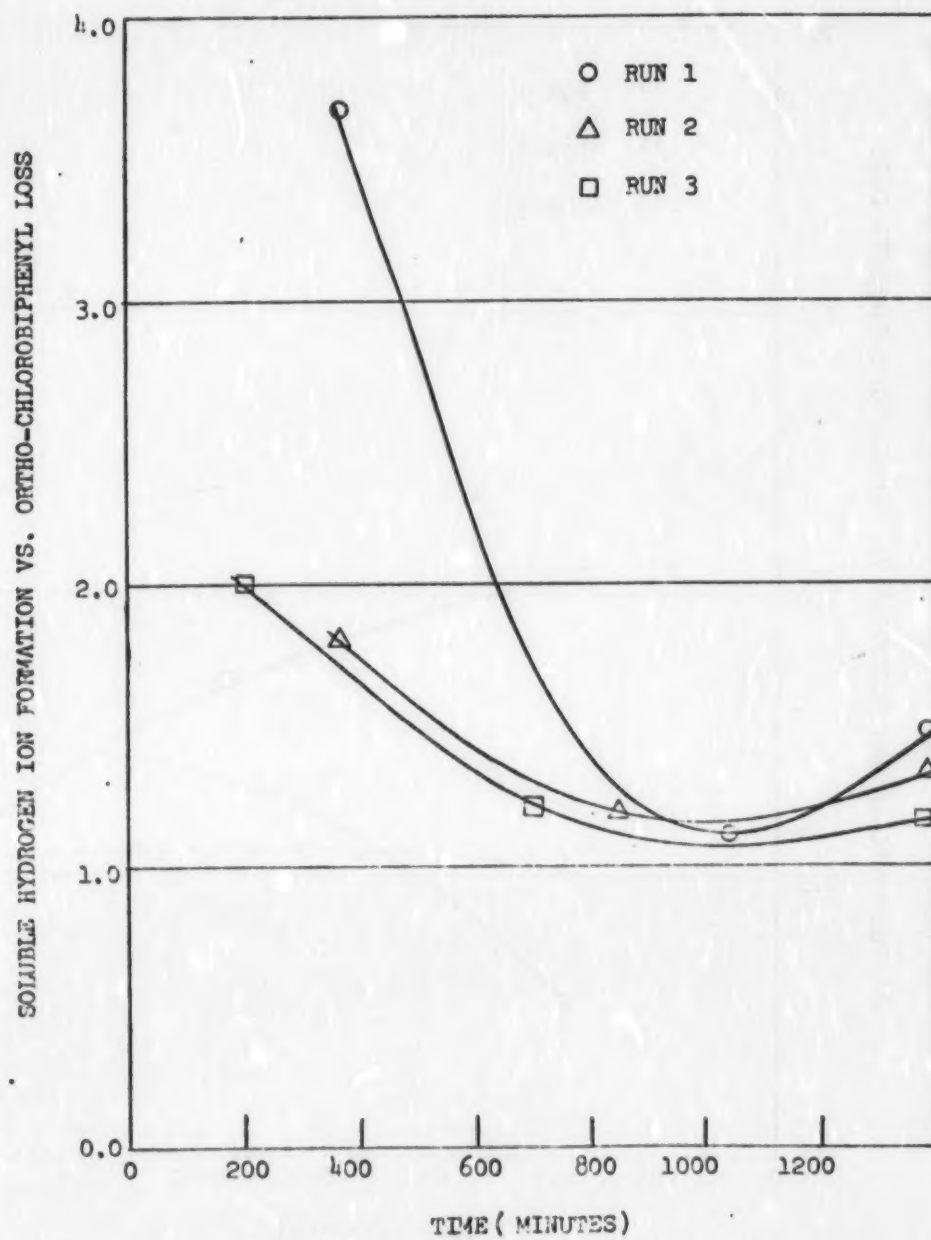


FIGURE 135

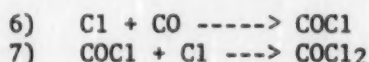
SOLUBLE HYDROGEN ION:ORTHO-CHLOROBIPHENYL LOSS VS. TIME IN
THE AIR/SIMULATED TROPOSPHERIC IRRADIATION.



The final data points, however, are in good agreement for H^+ and Cl^- . Due to the poor reproducibility of the earlier data points, however, it is difficult to discern any distinct trends between experiments. In general, OCB loss yields a quantitative conversion (50-100%) to HCl .

Irradiations of OCB in the presence of nitrogen dioxide were made but are not included here because instrument problems rendered OCB analysis poor. However, it should be noted that phosgene, $COCl_2$, was measured at ppb levels after about 17 hours of irradiation. Phosgene, although not measured in the experiments presented here, is expected to be produced in air irradiations without NO_2 .

Phosgene probably accounts for a very small (less than 1%) fraction of the chlorinated product yield. It is expected that it is formed by the reaction of atomic chlorine with atmospheric carbon monoxide.



It is not surprising that phosgene is produced in such small yields since its formation required the collision of ClO and Cl which are both present at low concentrations. This contrasts with the formation of HCl which requires the collision of one chlorine atom with one available hydrogen. The available hydrogen could be from molecular hydrogen present at 0.5 or from hydrogen on other PCB molecules.

Oxygenated Products - Since a review of the literature revealed that the photodissociation of aromatic halides in an oxygen environment generally produces phenol, aldehydes, and polymers analyses for phenolics and aldehydes were performed⁽¹⁷⁸⁾.

Although a detailed aldehydes and phenolics analysis by gas chromatography was desired, this proved impractical. Phenolics are difficult to separate by gas unless first derivatized. Higher molecular weight aldehydes likewise are difficult to separate without decomposition and the low molecular weight aldehydes suffer low sensitivity with flame ionization detectors. Analyses for phenolics and aldehydes were thus performed by wet chemical methods. Unfortunately, these techniques are non-specific and in the case of the aldehydes methods, insensitive.

In the irradiations made in nitrogen at the fourfold 310 nanometer intensity, an average of 1.06 ppm aldehydes (at $HCHO$) remained at the end of the 24 hour irradiation. The phenolics peaked at 3 ppb in the first 300 minutes and were undetectable at the end of the irradiation (see Figure 136).

In the nitrogen irradiations made with the tropospherically balanced lamp array (1/4 the previous 310 nanometer intensity), aldehydes averaged 0.45 ppm (as $HCHO$) at the end of the irradiations. The phenolics again peaked at around 3 ppb but did not reach its maximum until 700 minutes (see Figure 137).

FIGURE 136

PHENOLICS FORMATION IN THE NITROGEN/FOURFOLD 310 NANOMETER
INTENSITY IRRADIATION.

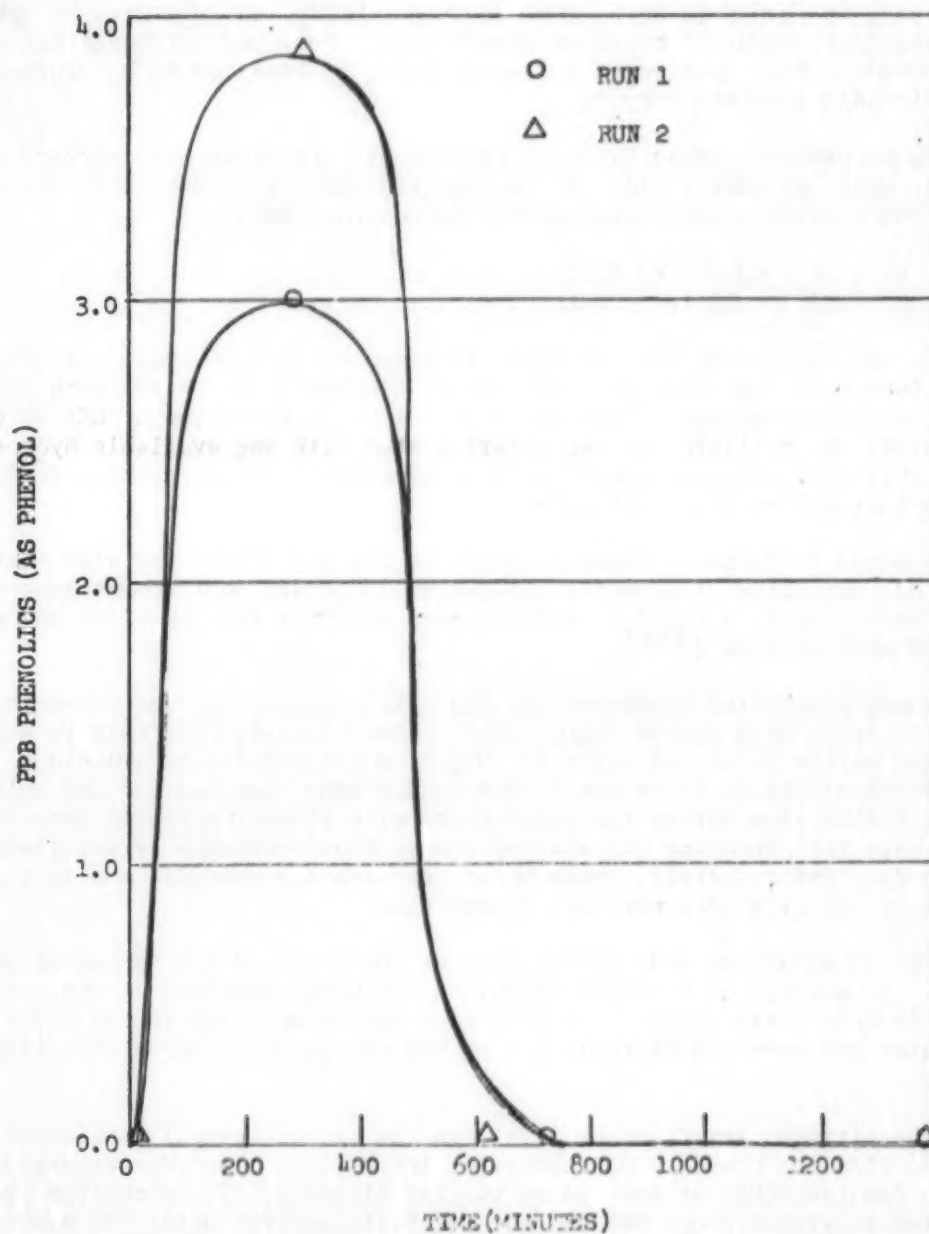
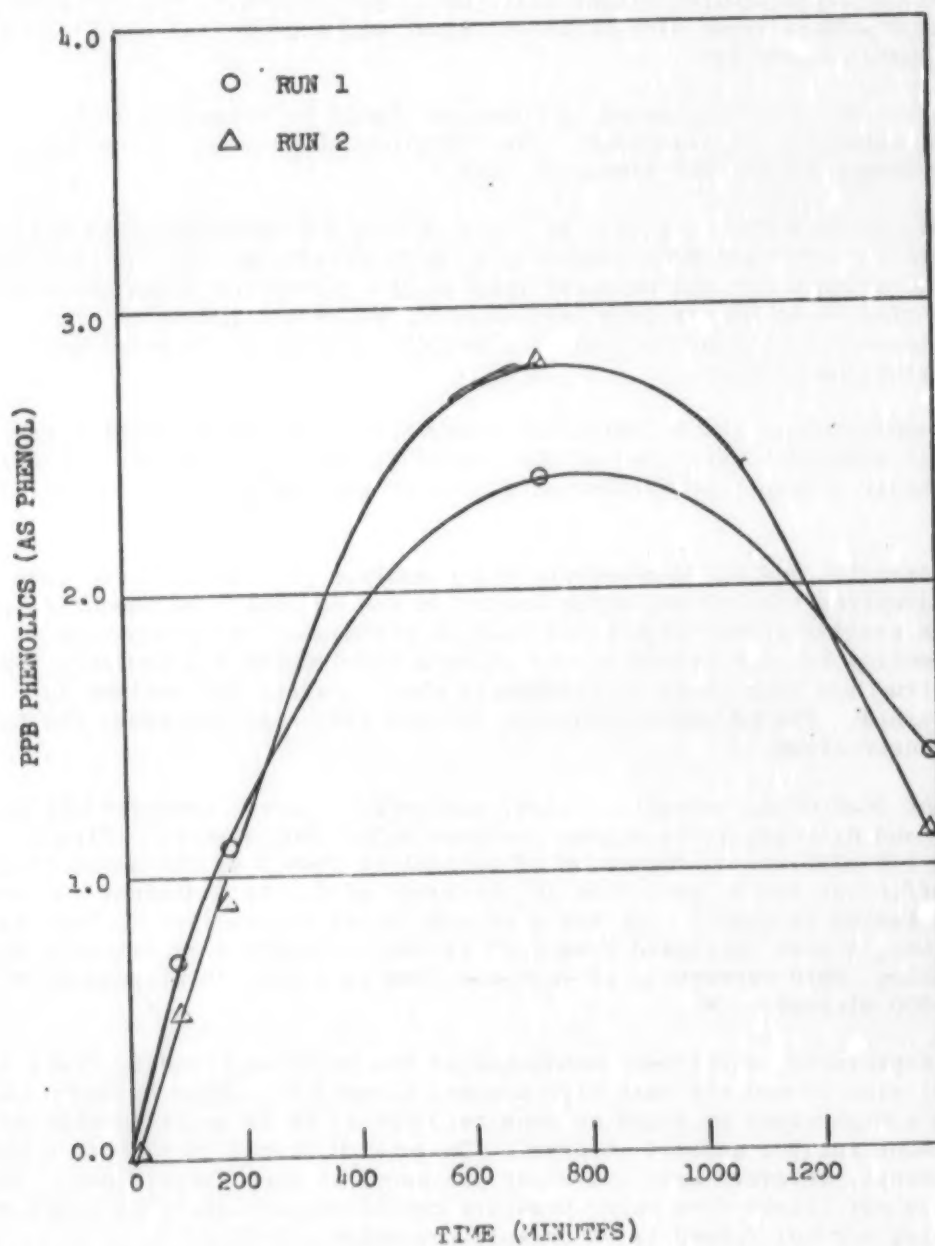


FIGURE 137

PHENOLICS FORMATION IN THE NITROGEN/SIMULATED TROPOSPHERIC
IRRADIATION.



In the air irradiations made with the same lamp balance, aldehydes averaged 0.37 ppm (as HCHO) at the end of the irradiations. The phenolics peaked around 200 minutes at about 1.5 ppb (see Figure 138).

It should also be noted that at the end of all irradiations, a characteristic aldehydic odor was evident. Although this was reminiscent of the odor of low molecular weight aldehydes, spot checks by gas chromatography with a flame ionization detector failed to reveal any C₂ to C₅ aliphatic aldehydes.

The results of the aldehyde production should be viewed in light of the photochemistry of aldehydes. The CHO group absorbs and dissociates the α hydrogen in the 310 nanometer band.

Thus, it is surprising that at the fourfold 310 nanometer intensity, there is more aldehydes remaining than is present at the same nitrogen irradiation under the balanced lamp array. Since the aldehydes would be expected to be higher with less than 310 nanometer radiation, the efficiency of the production of aldehydes is more efficient than its destruction process.

A comparison of the irradiations conducted in air vs nitrogen reveals lower aldehydes remaining at the end of the air irradiation. This is probably a result of further oxidation of aldehydes in the oxygen rich air.

Figures 136 and 137 demonstrate the phenolics profile observed upon quadrupling the 310 nanometer band. As can be seen, the phenolics peak much earlier at the higher 310 band in nitrogen. The production of phenolics is accelerated by the shorter wavelengths and probably its destruction rate since it disappears shortly after its maximum is attained. The presence of oxygen (Figure 138) also increases the rate of destruction.

Light Scattering Aerosol - Light scattering aerosol measurements on the air and nitrogen irradiations produced surprising results. Figures 139 and 140 exhibit the formation of aerosol expressed as the scattering coefficient due to particles in the range of 0.5 to 5 microns (molecular scattering is small). In terms of scattering coefficient in both irradiations, b scat increased from 0.23 to 100. Converted empirically to mass loading, this represents an increase from less than 10 micrograms/M³ to 3-5000 micrograms/M³.

An exploratory experiment conducted at low relative humidity (less than 10%) also showed the same high aerosol formation. Since hydrogen chloride has a high vapor pressure at room temperature it is unlikely that it would account for the aerosol observed. Oxygenated aromatics such as O-hydroxy-biphenyl, however, have low vapor pressures at room temperature. Thus, it is not likely from vapor pressure considerations that the light scattering aerosol formed is of organic character.

FIGURE 138

PHENOLICS FORMATION IN THE AIR/SIMULATED TROPOSPHERIC
IRRADIATION.

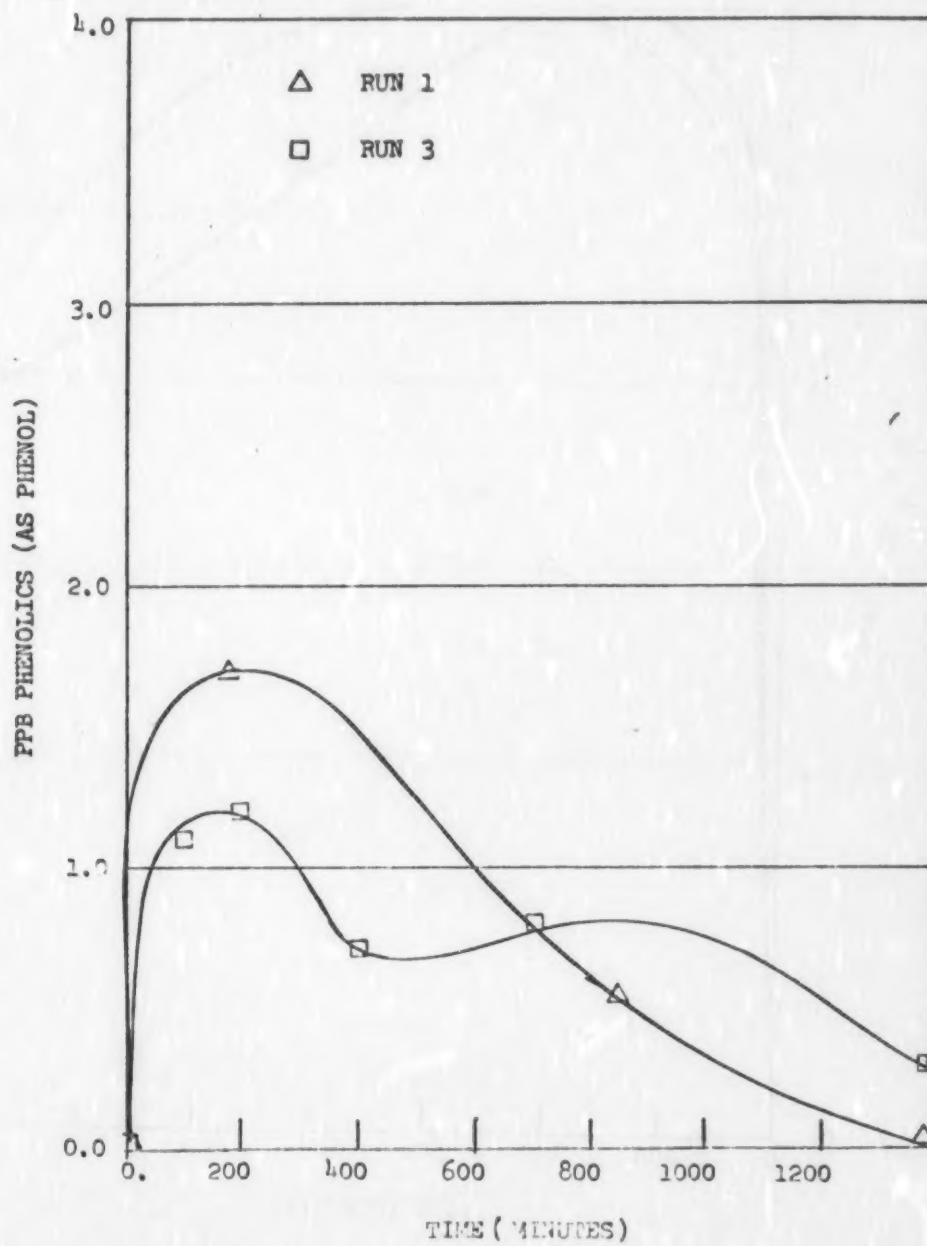


FIGURE 139

LIGHT SCATTERING AEROSOL FORMATION IN THE NITROGEN/
SIMULATED TROPOSPHERIC IRRADIATION (LOG B_{scat} VS. TIME).

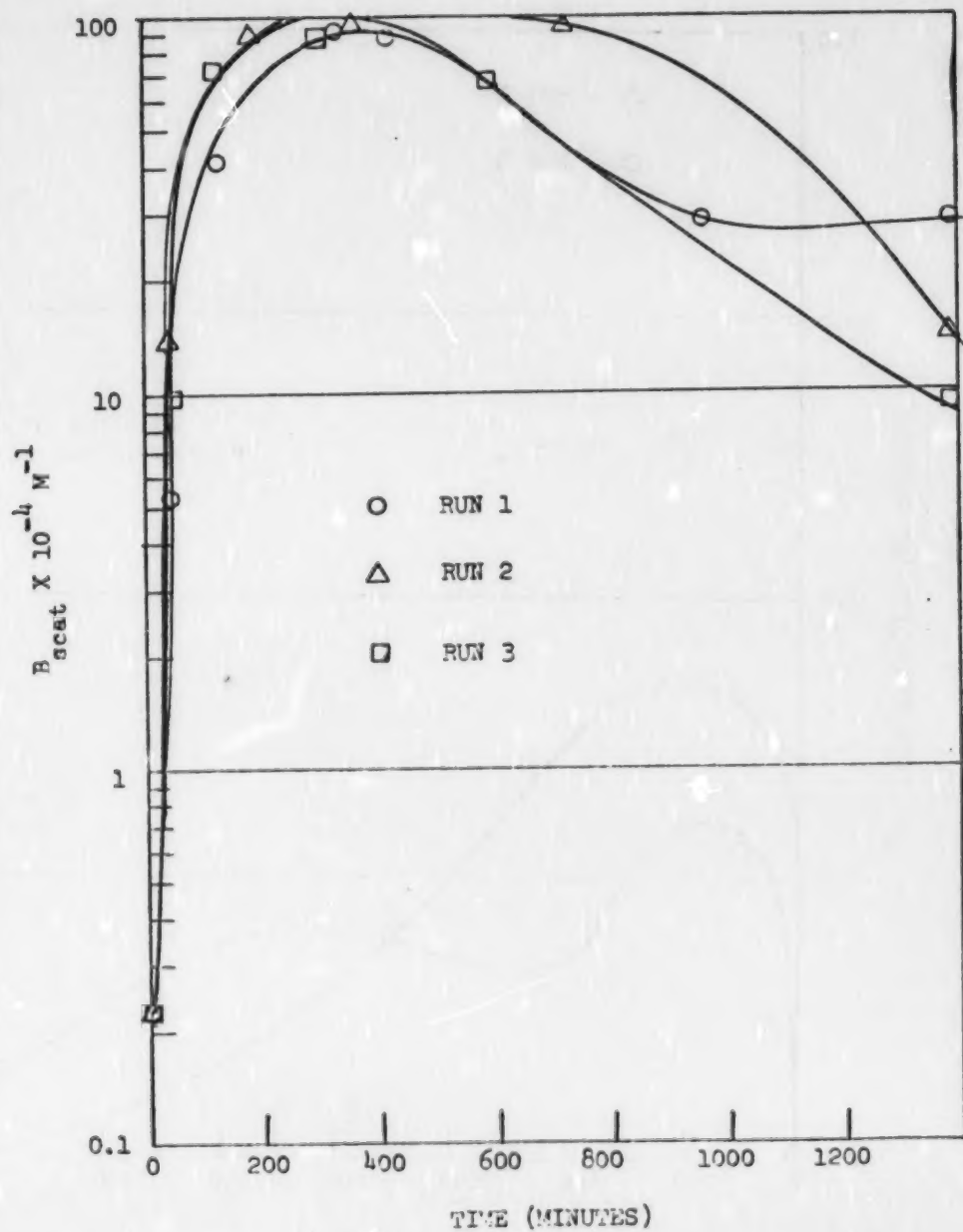
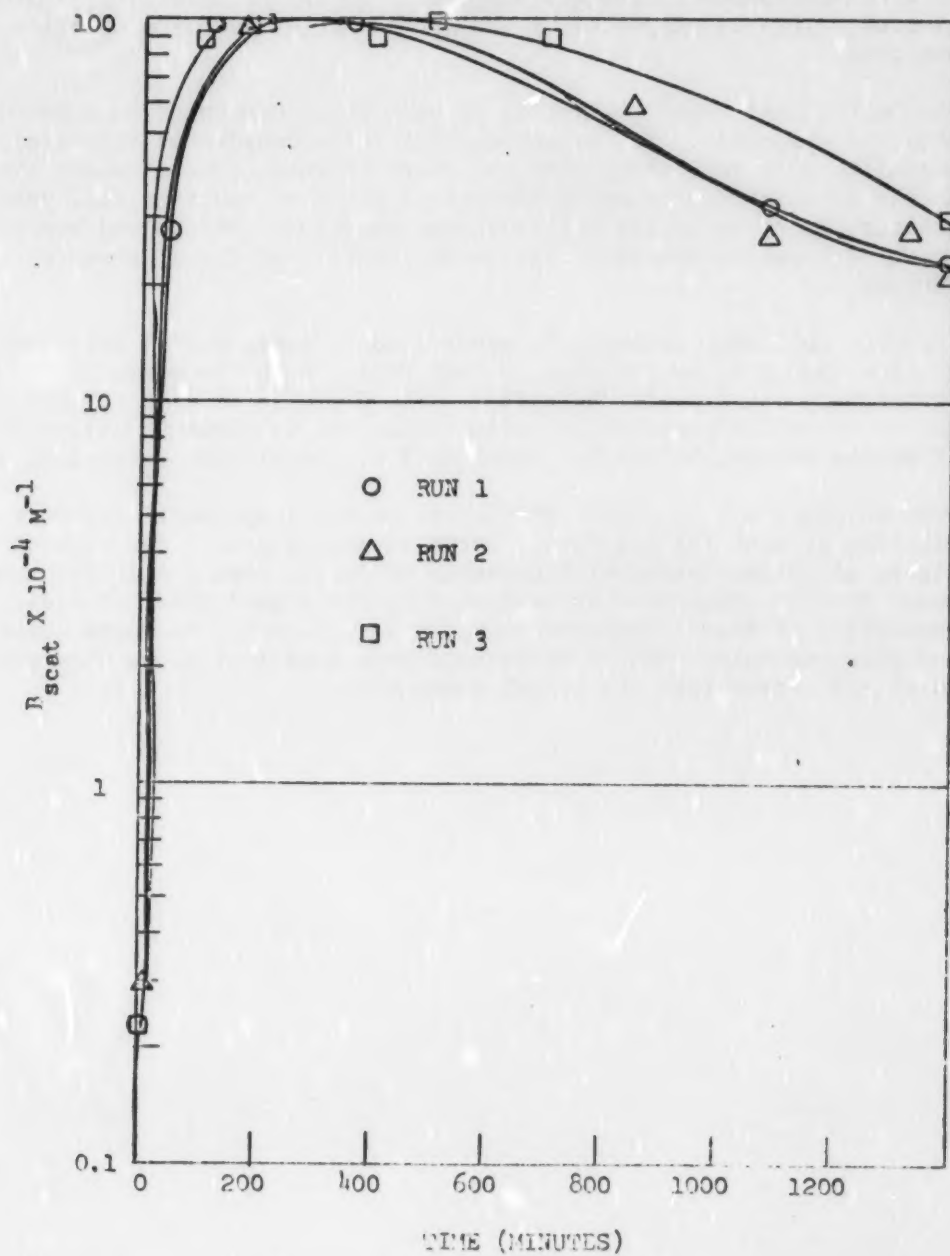


FIGURE 140

LIGHT SCATTERING AEROSOL FORMATION IN THE AIR/SIMULATED
TROPOSPHERIC IRRADIATION (LOG B_{scat} VS. TIME).



The results of this investigation indicate that 2-chlorobiphenyl is degraded in the troposphere through photochemical processes to mainly aldehydes and hydrogen chloride with minor yields of phenolics and phosgene.

The observed results indicate that the absorption of radiation of wavelengths between 290 nanometers to 310 nanometers leads to the degradation of 2-chlorobiphenyl. The weakest bond, the carbon-chlorine, is probably cleaved. This is supported by the appearance of hydrogen chloride and phosgene.

The bulk of the organic fraction appears to be converted to aldehydic and phenolic compounds. The detection of total aldehydes as collected by the bisulfite addition, along with the characteristic odor of short chain aliphatic aldehydes prompted efforts to pinpoint specific aldehydes. However, spot checks for acetaldehyde, propionaldehyde, and benzaldehyde produced negative results. The exact identity of the aldehyde(s) remains unknown.

Phenolic compounds detected in minor amounts representing less than 1% conversion appear to be transient. They build up in the early hours of the irradiation and die off thereafter. The decrease in concentration may be due to mechanical removal by condensation and subsequent settling. Also, it may be removed by further reaction i.e. photolysis, oxidation, etc.

From an overall view direct photolysis in the troposphere may be a very significant sink for the PCBs. Rates of disappearance for biphenyls of higher chlorine content will probably be faster than 2-chlorobiphenyl under similar conditions as evidenced by the liquid phase studies. The conversion of these compounds to aldehydes, phenols, hydrogen chloride, and phosgene makes removal by rainout more important since they are more soluble in water than the parent compounds.

LIST OF PUBLICATIONS AND THESES

1. "Absolute Determination of Phosgene: Pulsed Flow Coulometry" by A. Appleby, H.B. Singh, D. Lillian; Anal. Chem., 47, 860(1974).
2. "Fates and Levels of Ambient Halocarbons" by D. Lillian, H.B. Singh, A. Appleby, L. Lobban, R. Arnts, R. Gumpert, R. Hague, J. Toomey, J. Kazazis, M. Antell, D. Hansen, and B. Scott; A.C.S. Symposium Series, 17, 152(1975).
3. "Gas Chromatographic Methods for Ambient Halocarbon Measurements" by H.B. Singh, D. Lillian, A. Appleby, and L. Lobban; Env. Letters, (accepted for publication).
4. "Atmospheric Formation of Carbon Tetrachloride from Tetrachloroethylene" by H.B. Singh, D. Lillian, A. Appleby, and L. Lobban; Env. Letters, 10, 253(1975).
5. "Atmospheric Fates of Halogenated Compounds" by D. Lillian, H.B. Singh, A. Appleby, L. Lobban, R. Arnts, R. Gumpert, R. Hague, J. Toomey, J. Kazazis, M. Antell, D. Hansen, and B. Scott; Env. Sci. and Techn., 9, 1042(1975).
6. Comment on "Atmospheric Halocarbons: A Discussion with emphasis on Chloroform" by Y.L. Yung, M.B. McElroy and S.C. Wofsy; Geophys. Res. Letters, 3, 237(1976).
7. "Gas Chromatographic Analysis of Ambient Halogenated Compounds," by D. Lillian, H.B. Singh, and A. Appleby; J.A.P.C.A., 26, 141(1976).
8. "Atmospheric Formation of Chloroform from Trichloroethylene" by A. Appleby, J. Kazazis, D. Lillian, and H.B. Singh; Env. Letters, (accepted for publication).

Student Research Theses:

1. J. Kazazis, "Atmospheric Fates of Trichloroethylene and Ethylene Dichloride."
2. R. Gumpert, "An Investigation of the Ambient Behavior and Atmospheric Chemistry of Carbon Tetrachloride, Methyl Iodide and 1:1:1 Trichloroethane."
3. L. Lobban, "The Atmospheric Fates of C_2Cl_4 , CF_2Cl_2 and $CFC1_3$."
4. J. Toomey, "Atmospheric Fates of Vinyl Chloride and Methylene Chloride."
5. R. Arnts, "Photodegradation of Ortho-chlorobiphenyl under Simulated Tropospheric Conditions."

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